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Optically Active Hydrocarbon Polymers with Aromatic Side Chains

11. Dependence of Chiroptical Properties on the Distance Between Main Chain and Aromatic Group

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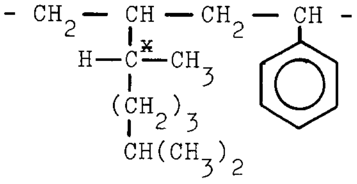
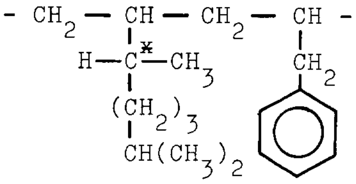
Dedicated to Prof. Dragutin Fleš on the occasion of his 60th birthday

Summary In a coisotactic copolymer of allylbenzene with (R)-3,7-dimethyl-1-octene(optical purity 95%), the phenyl chromophore shows appreciable dichroic bands. This indicates that the presence of a methylene group between phenyl and backbone does not exclude the asymmetric perturbation by the former. Molecular models and CD calculations suggest that the aromatic units can assume two different situations which cancel CD contribution by exciton dipole-dipole interactions between side chain phenyl groups.

Coisotactic random copolymers of optically active α-olefins with vinylaromatic monomers show chiroptical properties which are consistent with the inclusion of the aromatic units in helical sections with a predominant screw sense(CIARDELLI et al., 1972). In particular the CD arising from the electrically allowed $\pi\rightarrow\pi^*$ transition of the aromatic chromophore shows a couplet which has been related to the dipole-dipole interactions of the side chain aromatic chromophores, in a fixed chiral disposition. In the previously investigated copolymers the aromatic groups were directly attached to the main chain (I). It appeared then of interest to investigate



I



II

the chiroptical properties of the same chromophore con-

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nected to the main chain through a methylene group (II), as occurs for residues from natural aminoacids phenylalanine, tyrosine, histidine and tryptophane(CIARDELLI et al., 1978).

Coisotactic copolymers with structure II can be easily prepared by copolymerization of optically active 3,7-dimethyl-1-octene with allylbenzene in the presence of conventional Ziegler-Natta catalysts. Thus, by copolymerization of (R)-3,7-dimethyl-1-octene(optical purity 95%) and allylbenzene in 2/1 molar ratio in the presence of $TiCl_3/Al(\textit{i}.C_4H_9)_3$ (1/2) catalyst, the copolymer was obtained in 21% yield. Low molecular weight substantially atactic fractions were removed by extraction with boiling acetone. Successive extraction with diethylether gave a fraction containing 18% mole allylbenzene, which was substantially isotactic (NMR and IR). The diethylether extracted fraction was examined as it has comparable composition with the most investigated analogous styrene copolymer. The CD spectrum (*n*.heptane, room temperature, c = 0.15 ÷ 3.7 g/l, path cell = 0.1 ÷ 1 cm, Jobin-Yvon Mark III) of this sample showed dichroic bands in the region 270-185 nm where the ^1L_b, ^1L_a and ^1B transitions of benzene are located(JAFFE' and ORCHIN, 1962). A comparison with the analogous styrene copolymer(Fig. 1) indicates a substantial analogy apart the lower intensity, as far as the ^1L_b and ^1L_a bands are concerned. By contrast in the region of the high energy ^1B transition the styrene copolymer shows a negative couplet $|\Delta\varepsilon = -19.0(195\ nm)$ and $+10.9(188\ nm)|$, whereas the allylbenzene copolymer has only a negative band at 194 nm lower in intensity and no other bands are observed down to 185 nm. A similar CD behaviour had already been observed in the case of the conformational low molecular weight model (S)-2,2-dimethyl-3-phenyl-butane , where the exciton coupling was clearly not possible because of the presence of only one aromatic chromophore per molecule(SALVADORI et al., 1972). This last explanation cannot hold for the allylbenzene copolymers where the random distribution of the units is granted by the similar nature of the vinyl double bonds in the two comonomers.

Examination of molecular models indicates that allylbenzene units inserted in a 3_1-helix (III) can assume two conformations (IV) and (V) with the phenyl group eclipsing one or the other H-atom of the benzyl methylene group(Fig. 2).

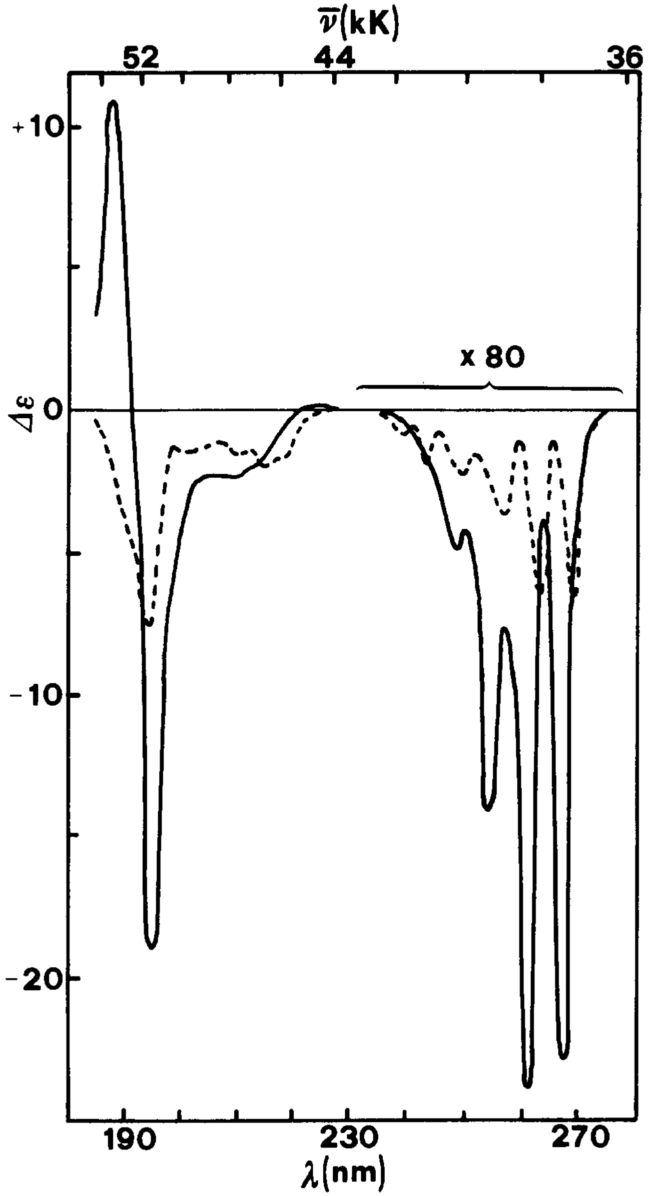
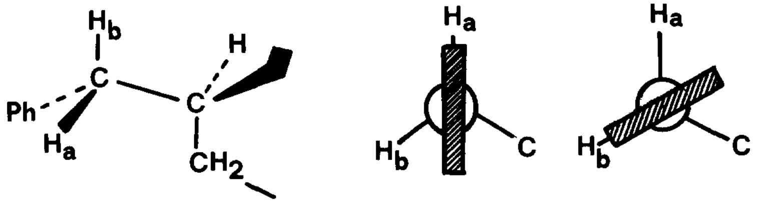


Fig. 1. CD spectra of styrene/(R)-3,7-dimethyl-1-octene (———) and of allylbenzene/(R)-3,7-dimethyl-1-octene(-----) copolymers in *n*.heptane solution at room temperature. The values of Δε are based on one aromatic residue.



III IV V

Fig. 2. Conformation of allylbenzene units in an isotactic right-handed 3_1-helix.

Even if IV and V are very probably not isoenergetic because of non-bonded steric interactions with other atoms of the chain, it is reasonable to assume that they are comparably populated. Thus, even if the allylbenzene units are inserted in an one screw sense helical chain, the regular array of aromatic groups with a fixed relative disposition can be interrupted by the random occurrence of both IV and V. As a consequence dipole-dipole interactions responsible of the CD couplets can be cancelled or strongly reduced.

In order to support this hypothesis calculations of CD spectra have been performed on the basis of the DE VOE (1965) model which has been successfully used in previous cases(HUG et al., 1974; CIARDELLI et al., 1977). This is a coupled oscillator theory of molecular optical properties and then, the relative geometry of the interacting chromophores as well as the description of their polarizability has to be provided. Lacking any other information, it has been assumed that the allylbenzene units(A) are inserted in a 3_1 helix(CORRADINI, 1968), with a right-handed screw sense[†], which is that induced by the chiral comonomer(B), having (R) absolute configuration(PINO et al., 1963). Cartesian coordinates of the atoms were obtained starting from standard bond lengths and angles. Following a previous procedure(HUG et al., 1974; CIARDELLI et al., 1977) the aromatic chromophore, in the spectral region of its electrically allowed ^1B transition, has been described by means of two oscillators, placed in the middle of the benzene rings and directed along two mutually orthogonal directions, in the plane of the benzene ring itself. The imaginary part of

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[†] The right-handed screw sense is that which moves away from the observer clockwise.

the polarizability for these oscillators was obtained from UV absorption spectra of toluene and the real part was generated from it by Kronig-Kramers transformation. As in previous cases, only tetrads have been considered containing at least two allylbenzene units, *i. e.*: AABB, ABAB, ABBA, AAAB, ABAA, AABA, AAAA. Clearly ABBB and BBBB cannot give any CD by coupling of aromatic units. The CD per 1 mole of A in the A/B(1:4) copolymer will be given(HUG et al., 1974; CIARDELLI et al., 1977) by:

$$\Delta\varepsilon = \frac{5}{4}\cdot\frac{1}{625}\,(\Delta\varepsilon_{AAAA} + 8\Delta\varepsilon_{AAAB} + 4\Delta\varepsilon_{AABA} + 4\Delta\varepsilon_{ABAA} + 48\Delta\varepsilon_{AABB} + 32\Delta\varepsilon_{ABAB} + 16\Delta\varepsilon_{ABBA})$$

assuming a purely random distribution of the two comonomers. It appears more likely in this case than in that of the styrene copolymer, because the two double bonds of allylbenzene and 3,7-dimethyl-1-octene are both purely aliphatic.

Owing to the occurrence of the conformational situations IV and V(Fig. 2), at least in principle, four situations are possible for each tetrad with two A units, eight for the tetrads with three A units and sixteen for the tetrad AAAA. In the Table, the calculated CD values for each of the above conformational situations are reported. These results show that the CD of each tetrad is very sensitive , as far as both sign and intensity are concerned, to the conformation IV or V assumed for every A unit in the tetrad itself.

Unfortunately, a correct resultant CD spectrum cannot be calculated from the above results, because the populations of the conformations IV and V are not known and then a complete comparison with the experimental data cannot be made. However, it is important to stress that the occurrence of couplets having opposite sign and comparable intensity, supports the possibility of a reduction(even a cancellation) of the dipole-dipole interaction contribution to the CD in this wavelength region. For instance, assuming that IV and V conformations are equally populated, the most probable tetrads capable of giving a CD couplet, *i. e.* those containing two A units, afford CD very low in absolute value and with opposite sign passing from AABB to ABAB tetrads(Fig. 3).

Note that ABBA tetrad gives zero CD at every wavelength (Table).

The CD data on the allylbenzene/(R)-3,7-dimethyl-1-octene copolymer allow to conclude that the presence of one

TABLE. Main features of the calculated CD curves in ^{1}B band spectral region for tetrads of allylbenzene(A)/(R)-3,7-dimethyl-1-octene(B) copolymer

Tetrad	$\Delta\varepsilon(\bar{\nu})$ [a]
AABB, BAAB, BBAA	+15(51.8), -11(54.6); -6(52.0), +5(53.8); -15(51.8), +11(54.6); +15(51.8), -11(54.6)
ABAB, BABA	+18(51.8), -14(54.6); -11(51.8), +9(53.8); +1(51.8), -1(53.8); -17(51.8), +12(54.6)
ABBA [b]	+9(52.0), -8(53.8); -9(52.0), +8(53.8)
AAAB, BAAA	+27(51.8), -18(54.6); -4(52.4), +4(54.6); +5(51.6), -3(53.0); -23(51.8), +15(54.6); +2(52.8), -3(55.0); +0.9(50.8), -1(51.8), +2(53.8), -2(55.0); +3(52.4), -4(54.6); +7(51.6), -6(54.6)
ABAA	+7(51.6), -4(54.6); +5(51.6), -6(53.4), +3(55.0); +16(51.4), -9(54.6); +8(51.8), -6(54.6); +15(51.4), -13(52.8), +5(54.8); +4(51.8), -3(53.4); -18(52.2), +14(54.6); -12(52.0), +13(54.8)
AABA	+9(51.6), -5(54.6); -13(51.4), +10(53.0); -5(51.8), +4(53.8); -13(52.2), +13(54.8); +16(51.4), -8(53.2); +21(51.8), -14(53.8); -15(52.0), +10(54.6); +3(51.4), -2(53.2)
AAAA	+13(51.8), -8(54.6); -1(51.2), +3(52.2), -1(53.8); +12(51.6), -8(54.6); +5(51.6), -5(53.0), +2(54.8); +11(52.4), -9(53.0), +3(55.0); -9(51.4), +5(53.2); -10(52.0), +9(54.6); -16(51.8), +14(54.6); +6(51.4), -2(53.2), -3(54.8); +8(51.6), -4(53.6); +5(51.4), -4(52.2), +2(53.8), -0.9(55.8); +2(51.6), -2(54.8); +16(51.4), -10(53.4); +15(51.8), -9(53.8); -10(52.2), +8(54.8); +1(51.4), -5(53.0), +4(54.8)

a) $\bar{\nu}$ expressed in kK.

b) Two other possible conformations gave zero at any energy in the ^{1}B range.

methylene group between main chain and phenyl groups weakens the contribution to CD by dipole-dipole exciton interactions of the aromatic chromophores.

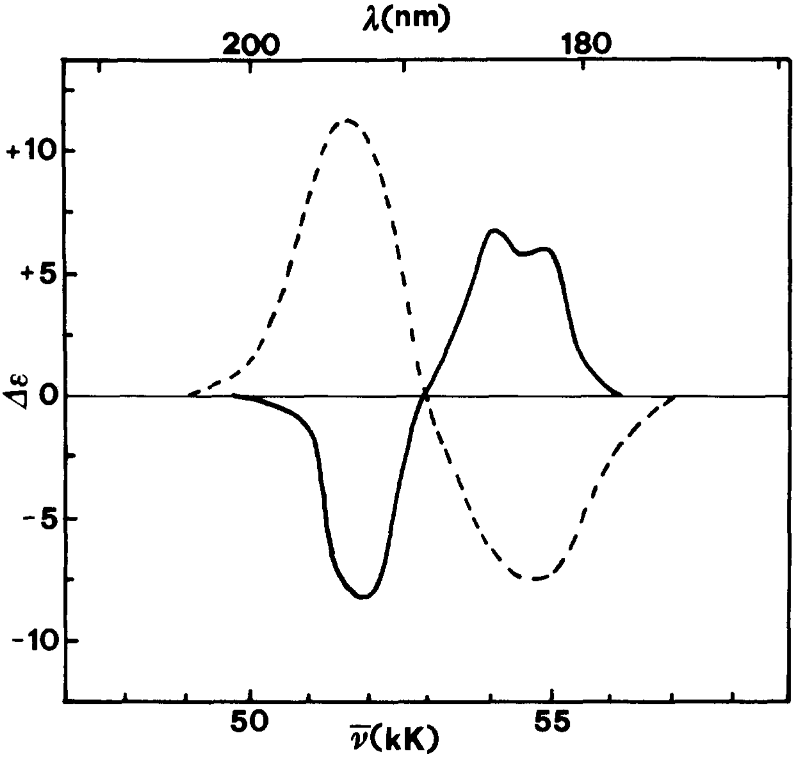

Fig. 3. Calculated CD spectra in the ^1B region for the tetrads containing two aromatic units assuming conformations IV and V equally populated(see text). (———) average value for ABAB and BABA tetrads; (-----) average value for AABB, BAAB and BBAA tetrads.

This result is due to the less homogeneous conformation of the aromatic units. Moreover an appreciable dissymmetric perturbation of the individual aromatic group by the main chain helical conformation is still observable as in the case of polypeptides containing aromatic α-aminoacids residues(CIARDELLI et al., 1978).

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