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CHIRALLY PERTURBED α-NAPHTHYL CHROMOPHORE IN HELICAL POLYMERS[+]

Francesco Ciardelli(*), Piero Salvadori, Carlo Carlini, Rita Menicagli, and Luciano Lardicci

Centro di Studio del C.N.R. per le Macromolecole Stereordinate ed Otticamente Attive - Istituto di Chimica Organica ed Istituto di Chimica Organica Industriale dell'Università, 56100 Pisa, Italy.

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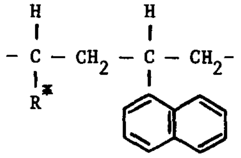
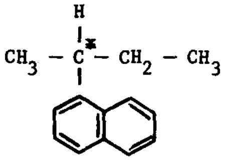
The chiroptical properties of the α-naphthyl chromophore have been not described up to now and no suitable optically active compounds containing this chromophoric moiety are readily available.

In previous papers we have reported that the copolymerization of styrene[1,2], or o.methylstyrene[2], with chiral α-olefins in the presence of stereospecific catalyst gives co-isotactic copolymers in which the $\pi \rightarrow \pi^*$ electronic transitions of the aromatic chromophore are optically active.

In order to test the general validity of the method and to obtain information on chiroptical properties of the α-naphthyl group we have investigated the stereoregular copolymers of α-vinylnaphthalene (I) with (S)-4-methyl-1-hexene (II) and (S)-3,7-dimethyl-1-octene (III), having 93.5% and 85.2% o.p., respectively. These co-isotactic copolymers (IV) have been prepared by highly stereospecific Ziegler-Natta catalysts obtained by reacting $TiCl_3$ "ARA" with $Al(C_2H_5)_3$ or $Al(\underline{i}.C_4H_9)_3$[3].



IV



V

($R^* = -CH_2\overset{*}{C}H(CH_3)C_2H_5$ in the I/II copolymer; $R^* = -\overset{*}{C}H(CH_3)\ (CH_2)_3CH(CH_3)_2$ in the I/III copolymer)

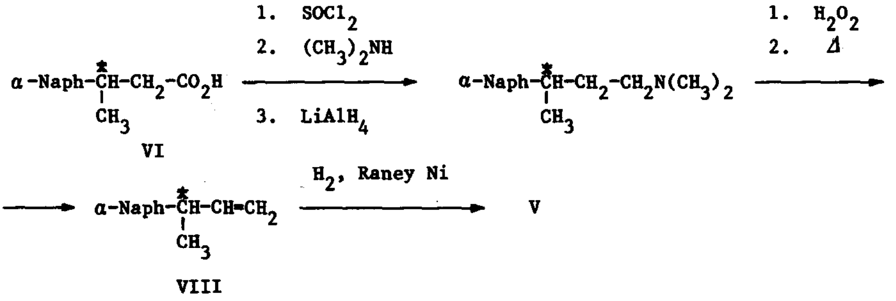
The absorption spectrum of the isotactic homopolymer of I, measured until to 250 nm in $CHCl_3$ because of its insolubility in hydrocarbon solvents, shows the maximum at 287 nm (ε_{max} ·

+) Paper VIII of the series "Optically Active Hydrocarbon Polymers with Aromatic Side Chains"; for paper VII see Ref.3.

= 5,850 based on one monomer unit) assignable to the L_a transition of naphthalene[4]. This band is flanked by a low intensity bands system at about 305 - 315 nm related to the L_b electronic transition [4] of the same chromophore.

Quite similar absorption spectra have been observed for the copolymers of I with both II and III. In the former case a sample containing 4% mol of aromatic units showed in its CD spectrum two structured optically active bands, the one between 325 and 295 nm with $\Delta\varepsilon_{max}$ (based on one monomeric unit from I) + 0.19 at 319 nm and the second between 295 and 265 nm with $\Delta\varepsilon_{max}$ - 0.14 at 275 nm. In the case of the I/III copolymer a sample with 36.1% mol units from I showed a similar CD spectrum in the same spectral region but with higher dichroic absorption, $\Delta\varepsilon_{max}$ being + 0.22 at 320 nm and -0.45 at 275 nm (Fig.1, IV-a). Moreover, thanks to the solubility in cyclohexane,absorption and CD spectra were recorded down to 200 nm. In the region of the ^1B_b electronic transition of the naphthalene chromophore[4,5] a strong absorption band is present with two evident maxima at 227 and 222 nm , ε_{max} being about 48,000 and 47,000, respectively; these values are both markedly lower than for the sharp band of naphthalene at 221 nm. Accordingly the CD spectrum shows a positive "couplet" with $\Delta\varepsilon_{max}$ + 53.5 and - 39.4 at 232 and 223 nm, respectively (Fig.1, IV-b).

We have prepared the low molecular weight model (+)(S)-2-(α-naphthyl)-butane (V)[6] following a new route suitable for the determination of the relationship between optical purity and rotatory power. (+)(S)-2-(α-naphthyl)-butanoic acid[6] (VI) was converted into V as reported in the following scheme:



$$\alpha\text{-Naph-}\overset{*}{C}H(CH_3)\text{-}CH_2\text{-}CO_2H \xrightarrow[3.\ LiAlH_4]{1.\ SOCl_2\quad 2.\ (CH_3)_2NH} \alpha\text{-Naph-}\overset{*}{C}H(CH_3)\text{-}CH_2\text{-}CH_2N(CH_3)_2 \xrightarrow{1.\ H_2O_2\quad 2.\ \Delta}$$

$$\xrightarrow{} \alpha\text{-Naph-}\overset{*}{C}H(CH_3)\text{-}CH{=}CH_2 \xrightarrow{H_2,\ Raney\ Ni} V$$

VI

VIII

The relationship between rotatory power and optical purity of VIII was established by oxidative degradation[7] to (R)-2-(α-naphthyl)-propionic acid and assuming for this acid ($[\alpha]_{D\,max}^{25}$ 145.9, acetone)[8]. Moreover, excluding appreciable racemization in the catalytic reduction of VIII it was possible to attribute to the sample of V recovered ($[\alpha]_D^{25}$+ 18.49, neat) the same minimum optical purity as the corresponding olefin (71.6%).

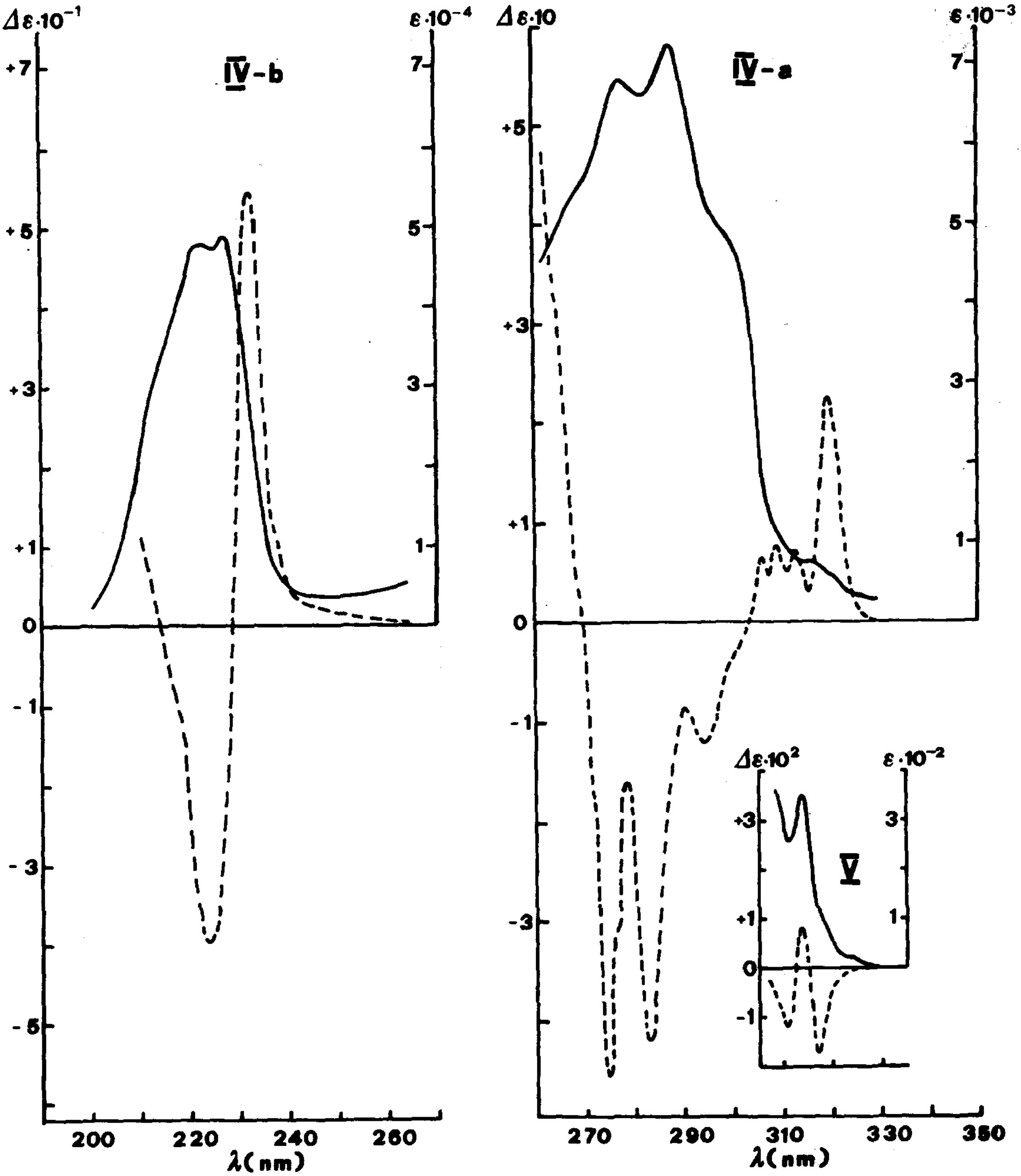


Figure 1. UV (——) and CD (---) spectra of the α-vinylnaphthalene/(S)-3,7-dimethyl-1-octene copolymer (IV-a and IV-b) and of (S)-2-(α-naphthyl)-butane (V) in saturated hydrocarbon solution. (In IV-a and IV-b ε and $\Delta\varepsilon$ are based on one monomer unit derived from α-vinylnaphthalene; see Ref.2 footnote 9).

The UV spectrum of V is very similar to that of naphthalene with a single band in the ^1B_b region, ε_{max} being 94,500 at 225 nm. The high dissymmetry factor did not permit the detection of optically active bands above 300 nm. An optically active band system could be however observed in the region of ^1L_b electronic transition of naphthalene, the dichroic absorption being 20 to 30 times lower than in the copolymers (Fig.1, V). This result can be primarily interpreted by assuming a larger conformational homogeneity in the copolymer than in V. Isotactic poly-α-vinyl-naphthalene (poly-I) macromolecules assume a helical conformation in the crystalline state[9]; it is reasonable to suppose that the same is true for the copolymers, the chiral comonomer II or III with S absolute configuration favouring the left-handed screw sense[10]. The local dissymmetric perturbation of a single aromatic group can give CD bands of the same order of magnitude as in the copolymers, if an appreciable conformational rigidity [11] is provided. However, dipole-dipole interactions between α-naphthyl groups bound with a fixed mutual geometrical disposition along the helical chain can supply additional rotatory strength to the electronic transitions, and particularly to those having larger polarizability[12]. This seems to be substantiated by the couplet in the 230-220 nm region. It is worth mentioning that the same correlation was observed between sign of the couplet and predominant screw sense in the analogous copolymers of styrene and o.methylstyrene[2], a positive couplet indicating the prevalence of a left-handed helical conformation.

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REFERENCES

1. P.Pino, C.Carlini, E.Chiellini, F.Ciardelli, and P.Salvadori, J.Amer.Chem.Soc., 90, 5025 (1968).
2. F.Ciardelli, P.Salvadori, C.Carlini, and E.Chiellini, J.Amer.Chem.Soc., 94, 6536 (1972).
3. C.Carlini and E.Chiellini, Makromol.Chem., 176, 519 (1975).
4. H.B.Klevens and J.R.Platt, J.Chem.Phys., 17, 470 (1949).
5. T.Hoshi, J.Yoshino, H.Fumani, H.Kadoi, and H.Inoue, Ber.Bunsen-Gesellschaft, 76, 888 (1972).
6. R.Menicagli, L.Lardicci, and C.Botteghi, Chem. & Ind., 920 (1974).
7. L.Lardicci and R.Menicagli, J.Org.Chem., 37, 1060 (1972).
8. A.Fredga, Arkiv Kemi, 8, 463 (1955).
9. P.Corradini and P.Ganis, Nuovo Cimento, Suppl., 15, 104 (1960).
10. P.Pino, F.Ciardelli, G.P.Lorenzi, and G.Montagnoli, Makromol.Chem., 61, 207 (1963).
11. P.Salvadori, L.Lardicci, R.Menicagli, and C.Bertucci, J.Amer.Chem.Soc., 94, 8598 (1972).
12. W.Hug, F.Ciardelli, and I. Tinoco, Jr., J.Amer.Chem.Soc., 96, 3407 (1974).