Polymer Bulletin 13, 469–472 (1985)

Polymer Bulletin

Vacuum-u.v. Circular Dichroism of Optically Active Isotactic Poly-α-Olefins

Carlo Bertucci, Piero Salvadori, Francesco Ciardelli, and Graziella Fatti

Centro di Studio del C.N.R. per le Macromolecole Stereordinate ed Otticamente Attive, Dipartimento di Chimica e Chimica Industriale, Università di Pisa, I-56100 Pisa, Italy

Summary. Circular dichroism of isotactic samples of poly-(S)-4-methyl-1-hexene and poly-(R)-3,7-dimethyl-1-octene, have been measured in the vacuum ultraviolet spectral region (200-140 nm). The c.d. band at about 160 nm accounts for the optical activity in the visible region and reflects the presence of one screw sense helical conformation of the sample examined.

The isotactic polymers derived from optically active α-olefins assume, in general, helical conformation of a single screw sense in the crystalline state (1). Some experimental evidences have been obtained suggesting that such an ordered structure is mantained in solution at least for sections of macromolecular chain. In particular, optical rotatory dispersion (o.r.d.) studies on isotactic polymers of α-olefins with an asymmetric carbon atom in the 1 and 2 position to the double bond (such as 3-methyl-1-pentene, 3,7-dimethyl-1-octene and 4-methyl-1-hexene) and low molecular weight paraffins (2-5), acting as structural and conformational models, indicated high conformational homogeneity of the macromolecular compounds due to the one screw sense helicity of the backbone. In both polymers and models the rotatory power followed strictly an one term Drude equation $\{|\Phi|_\lambda = =K/(\lambda^2 - \lambda_0^2)\}$, with the rotatory constant (K) assuming different values while λ_0 was the same (about 165 nm), quite close to that of the lowest energy transition (159 nm) estimated for an infinite linear hydrocarbon chain (6). Because of the location of this last transition c.d. investigation by commercially available instruments was not allowed for poly-α-olefins, and an aromatic chromophore as conformational c.d. probe was introduced by preparing coisotactic copolymers of the above chiral olefins with vinyl aromatic monomers like styrene, 1- and 2-vinylnaphthalene and allylbenzene (7-10).

As one of the c.d.machines which can work down to the vacuum u.v. region (11) became accessible to us, it was possible to investigate the c.d. of isotactic samples of poly-(S)-4-methyl-1-hexene, 1, and poly-(R)-3,7-dimethyl-1-octene, 2, prepared following known procedures (2).

The c.d. spectra (figures 1a and 2a) have been recorded between 200 and 140 nm on polymer films obtained by slow evaporation of a diluted solution. One positive band (λ_{max} 158 nm, $\Delta\varepsilon_{max}$ +3, per monomeric unit) and the beginning of a second positive band ($\lambda_{max} < 140$ nm) have been observed in the c.d. spectrum of 1. The wavelength of the maximum of the c.d. is in good agreement with the value extrapolated (λ_0) by one term Drude equation of the o.r.d. curve of 1 in hydrocarbon solution (165 nm) and in the crystalline state (162 nm) (12). These experimental c.d. data were used for calculating the o.r.d. curve by Kronig-Kramers transform (13) which resulted in good agreement, at least for the sign and the order of magnitude, with the experimental o.r.d. curves recorded for the same polymer in solution

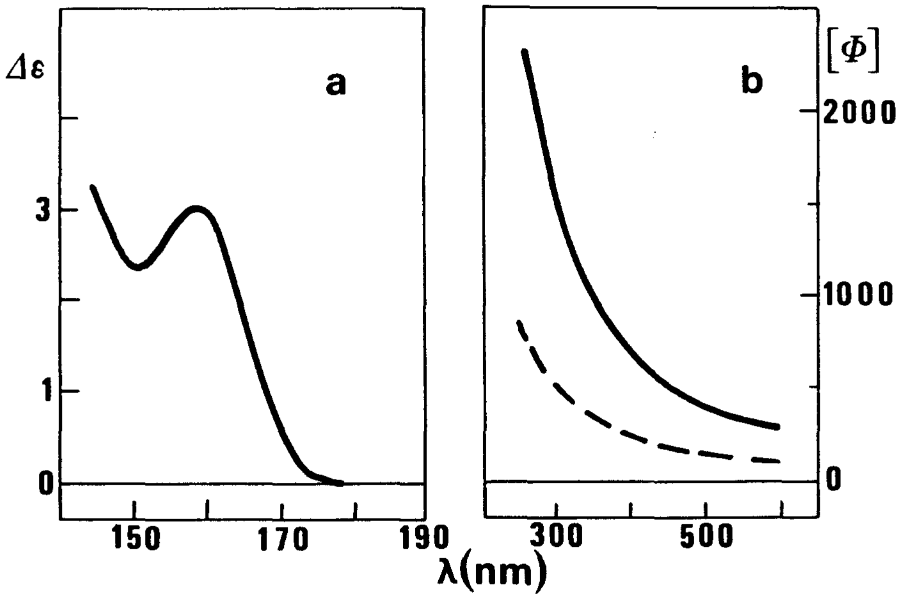

Figure 1 - a. c.d. curve of 1 on film;
b. o.r.d. curves of 1 in hydrocarbon solution (——) and calculated from c.d. data a. (---)

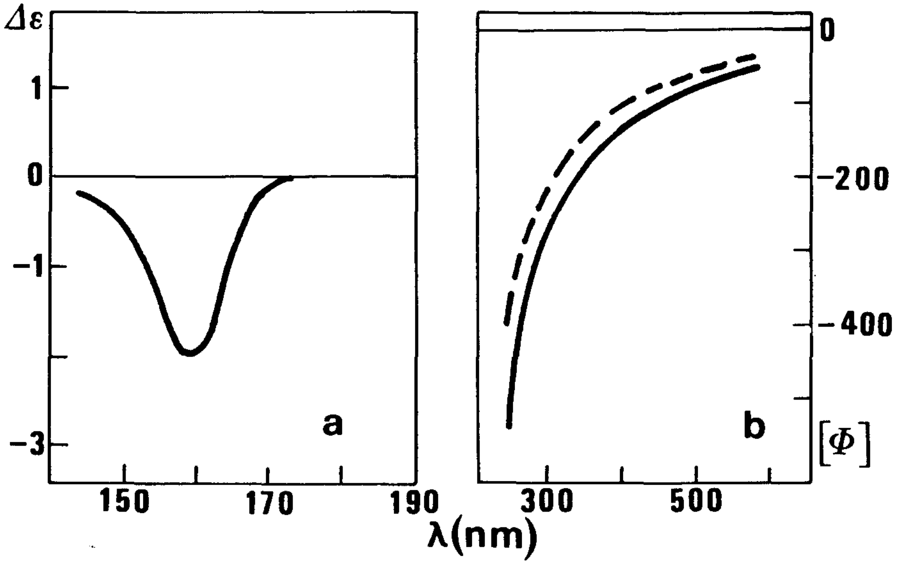

Figure 2 - a. c.d. curve of 2 on film;
b. o.r.d. curves of 2 in hydrocarbon solution (——) and calculated from c.d. data a. (---)

and in the crystalline state (Figure 1b). In this last state the chiroptical properties of 1 are depending on crystallinity degree since this polymer in general crystalizes in both right and left handed helical conformations, as the polymers from (R,S)-4-methyl-1-hexene. Then the crystalline state chiroptical properties are usually lower, in absolute value, than in solution, as crystallization in one screw sense helices can be obtained only under very special conditions (12). Only one c.d. band has been observed in the case of 2 (Figure 2a) where again the maximum has been detected at 158 nm ($\Delta\varepsilon_{max}$ -2, per monomer unit). The energy position of the c.d. band is in reasonable agreement with the extrapolated λ_0 value (174 nm, hydrocarbon solution; 173 nm, crystalline state) by one term Drude equation (12). The o.r.d. curve calculated by Kronig-Kramers transform from c.d. data fit very well (Figure 2b) with the experimental o.r.d. curve; indeed the macromolecules of 2, assume in the crystalline state an one screw sense helical conformation. It is worth noting that only one c.d. band has been observed between 200 and 140 nm also in the case of optically active low molecular weight paraffins; indeed the c.d. spectrum of (3S,5S)-2,2,3,5-tetramethylheptane (14) presents only one c.d. band centered at about 150 nm. Accordingly the o.r.d. curve follows a one-term Drude equation with an extrapolated λ_0 value of 170 nm.

In conclusion, vacuum u.v. c.d. data and the good agreement between the experimental and calculated o.r.d. curves for both 1 and 2 indicate that the optical rotation of isotactic poly-α-olefins as well as of low molecular weight paraffins is mainly determined by the electronic transition allied to the c.d. band at about 160 nm, thus confirming unequivocally that differences in chiroptical properties are due to a different position of conformational equilibrium and not to new electronic transitions connected to the macromolecular structure. This last conclusion is also supported by the lack of peculiar c.d. features, such as the couplet observed for example in the case of (R)-3,7-dimethyl-1-octene/styrene copolymer (7), to be related to the ordered secondary structure of the macromolecules in solution. Finally the good agreement between the experimental wavelength of the maximum of the c.d. band and the extrapolated value, indicates that the one screw sense helicity of the polymer chain can be related directly to the intensity of the c.d. band observed at about 160 nm and consequently to the value of the optical rotatory power.

Experimental section

C.d. measurements. C.d. spectra were recorded with a vacuum ultraviolet spectrometer at the Department of Biochemistry and Biophysics, Oregon State University, Corvallis, Oregon, and carried out on films by using CaF_2 windows from Frank Cook Inc. Films of the polymers were obtained by slow evaporation of the solvent from a dilute (c < 1 g/L) solution of the samples dissolved in hydrocarbons or in chlorinated solvents. The values reported represent an arithmetic average of at least six measurements. All the films were tested to exclude any orientation dependence of the c.d. signals. In all cases the total optical density was kept below 1.0. The spectral slit width was a constant 1.6 nm.

Synthesis of polymers. According to procedures reported in the literature, the polymerization of (S)-4-methyl-1-hexene (optical purity 93.7%) and (R)-3,7-dimethyl-1-octene (optical purity 96%) was carried out in similar way by using, respectively, $Al(i\text{-}C_4H_9)_3/TiCl_4$ and $Al(i\text{-}C_4H_9)_3/TiCl_3$ as catalytic systems. The molar ratios of the metal alkyl and of the monomer to the transition metal halides were 3 and 30, respectively. The crude solid methanol insoluble polymers were extracted by boiling solvents, obtaining four polymer fractions having different stereoregularity and optical rotation. Measurements were performed on the fractions extracted with diethylether and cyclohexane which are known to be substantially isotactic (2) {1, $|\alpha|_D^{25}$ +264.1 (c 0.30, cyclohexane, diethylether fraction); $|\alpha|_D^{25}$ +278.8 (c 0.03, cyclohexane, cyclohexane fraction). 2, $|\alpha|_D^{25}$ -76.4 (c 0.54, chloroform, diethylether fraction); $|\alpha|_D^{25}$ -89.6 (c 0.13, carbon tetrachloride, cyclohexane fraction)}.

The authors thank Prof.W.C.Johnson, Jr., Department of Biochemistry and Biophysics, Oregon State University, for allowing them to use the vacuum u.v. spectrometer. This work has been partially supported by a N.A.T.O. grant, and by Ministero Pubblica Istruzione (MPI), Roma - Italy.

References

1. V.Petraccone, P.Ganis, P.Corradini, G.Montagnoli, Eur.Polymer J., 8, 99 (1972).
2. P.Pino, F.Ciardelli, G.P.Lorenzi, G.Montagnoli, Makromol.Chem., 61, 207 (1963).
3. P.Pino, P.Salvadori, E.Chiellini, P.L.Luisi, Pure Appl.Chem., 16, 469 (1968).
4. P.Pino, Adv.Polym.Sci., 4, 393 (1965).
5. P.Pino, F.Ciardelli, M.Zandomeneghi, Ann.Rev.Phys.Chem., 21, 2520 (1970).
6. J.W.Raymonda, W.T.Simpson, J.Chem.Phys., 47, 430 (1967).
7. F.Ciardelli, P.Salvadori, C.Carlini, E.Chiellini, J.Amer.Chem.Soc., 94, 6536 (1972).
8. W.Hug, F.Ciardelli, I.Tinoco, Jr., J.Amer.Chem.Soc., 96, 3407 (1974).
9. F.Ciardelli, C.Righini, M.Zandomeneghi, W.Hug, J.Phys.Chem., 81, 1948 (1977).
10. C.Bertucci, C.Carlini, F.Ciardelli, C.Rosini, P.Salvadori, Polymer Bulletin, 5, 535 (1981).
11. W.C.Johnson, Jr., Ann.Rev.Phys.Chem., 20, 93 (1978).
12. O.Bonsignori, G.P.Lorenzi, J.Polymer Sci., A-2, 8, 1639 (1970).
13. W.Moffit, A.Moscowitz, J.Chem.Phys., 30, 648 (1959).
14. S.D.Allen, O.Schnepp, J.C.S. Chem.Comm., 904 (1974).

Accepted May 13, 1985

C