

STRUCTURAL ANALYSIS OF OPTICALLY ACTIVE COPOLYMERS BY CD

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Abstract - Copolymerization of an optically active monomer with a non chiral comonomer gives rise in general to copolymer macromolecules showing dichroic bands in the absorption region of chromophores present in the latter comonomer. This "induced optical activity", attributed to the dissymmetric conformation assumed by the copolymer chains, is dependent on monomers structure, stereoregularity, composition and sequence distribution. Proper comonomer selection allows to obtain polymeric products containing dissymmetrically perturbed functional groups in a simple and economical way. Conversely CD can be used for unequivocally proving copolymer formation and for sophisticated conformational studies in solution by introducing chiral probes in the chains.

INTRODUCTION

It is well known that optical activity is very sensitive to conformational variations; accordingly chiroptical techniques (ORD and CD) have been widely used to investigate conformational equilibria of organic compounds, mainly in solution(1). Theoretical interpretation of optical activity is very complex and satisfying theories are not yet available(2).

In this connection polymers, because of the linear repeating structure, offer some advantages and can be approached by semiempirical methods which allow evaluation of the basic chiroptical properties of regular secondary structures(3); typical examples are offered by proteins(4) and also nucleic acids(5).

While natural polymers, with the exception of natural rubber, are optically active and can thus be studied directly with chiroptical techniques, this is not the case for most synthetic polymers, particularly vinyl polymers. In these polymers, therefore at least the natural circular dichroism(CD) is observable only if optically active materials are used at synthetic

level either as monomers or catalysts(6). Obtaining optically active monomers, particularly with high enantiomeric purity, is in general cumbersome and very expensive. The apparently most convenient use of optically active catalysts and racemic or prochiral monomers gives a good optical yield only in few cases(7,8).

On the other hand, basic investigation on synthetic optically active polymers(9), particularly stereoregular ones, has shown that ordered secondary structures can exist in solution displaying often much larger optical activity than low molecular weight structural models.

As the ordered structure finds its stability in cooperative steric effects between monomeric units along the chain, these studies suggested two lines of development:

- i) Investigation of conformation in solution of synthetic polymers by means of suitable chromophores inserted in or attached to the macromolecule to act as chiral conformational probes.
- ii) Simple and economic synthesis of optically active materials by inserting in the same chain chiral groups and functional moieties.

Both points deal clearly with copolymers and are of interest for two distinct application areas, the former concerned with structural analysis and the latter with synthesis of new materials.

The existence of the above "cooperative conformational effect" was firstly demonstrated in the case of stereoregular α -olefin copolymers. Thus the coisotactic copolymers of (S)-4-methyl-

1-hexene with 4-methyl-1-pentene showed much larger optical rotation than the corresponding copolymer mixtures indicating that the units from achiral 4-methyl-1-pentene assumed in the copolymer macromolecules conformations of a predominant chirality(10). Investigation of these olefin copolymers by CD was not possible as paraffins absorb below 160 nm(11), a region which cannot be reached by the commercially available instruments.

On the other hand CD has been very useful when moving to polymers containing chromophoric groups in an accessible spectral region. The absence of tails in dichroic bands allow in general a good resolution between contributions of the two comonomers, provided they contain groups absorbing in two distinct regions. The basic work in this area has been done with copolymers of α -olefins and vinyl aromatic monomers; the units from the former absorb, as said, below 160 nm, whereas the aromatic π electrons of the latter are characterized by electronic transitions over 190 nm(12). The topic has been recently reviewed(13) and we summarize here the main conclusions which are useful in the analysis of the more complicated systems reported in the following sections. Certainly copolymers of optically active α -olefins with vinyl aromatic hydrocarbons are unique in the context of this paper, as they can be obtained with a very high isotacticity degree in the presence of Ziegler-Natta catalysts and the aromatic chromophore is the only absorbing moiety over 180 nm thus strongly simplifying the analysis of CD spectra. These particular properties allowed the following conclusions:

- a- In coisotactic copolymers of styrene, methyl styrene derivatives, 1- and 2-vinylnaphtalene with optically active α -olefins having general formula $\text{CH}_2=\text{CH}(\text{CH}_2)_n^* \text{CH}(\text{CH}_3)\text{R}$ ($n = 0-2$ and $\text{R} = \text{alkyl}$) strong dichroic bands are found corresponding to absorptions of the aromatic π -electrons system.
- b- The "induced CD" of the aromatic chromophore increases with stereoregularity and content of optically active monomer up to an asymptotic value.
- c- Larger asymmetric effect is observed when the asymmetric carbon atom of the olefin is closer to the main chain.
- d- The "induced CD" arises from local site dissymmetric perturbation and from exciton coupling between chromophores of different units in the one screw sense helical chains.

Taking into account the above points we wish to discuss in this paper recent examples concerning copolymers of two functional monomers, only one of which is optically active. Because of space reasons we will limit ourselves to polymers with a hydrocarbon main chain which allows us to concentrate analysis on chromophoric side chains.

COPOLYMERS OF VINYLAROMATIC HYDROCARBONS WITH (-)-MENTHYL ACRYLIC ESTERS

Styrene (St)(14,15), 1-vinylnaphtalene (1VN)(16), and 6-vinylchrysene (6VC)(17), have been copolymerized in the presence of free radical initiators with (-)-menthylacrylate (MtA) or -methacrylate(MtMA) both absorbing below 220-230 nm, whereas the longest wavelength absorption band of the aromatic chromophores is located at a wavelength larger than 250 nm.

Optical rotation of all these copolymers linearly depends on composition thus apparently excluding any dissymmetric effect of menthyl groups on the aromatic units (Fig. 1).

However CD spectra show appreciable dichroic bands in the region where the different aromatic chromophores only have absorption bands (Figs.2 and 3).

The copolymers of styrene with (-)-menthylacrylate [poly(MA-co-St)] have been investigated in detail as far as the lowest energy absorption band, corresponding to the 1L_b transition of benzene, is concerned. This last is located between 250 and 280 nm (Fig. 2) well out of the region of the ester chromophore absorption which is below 225 nm(18) and can act as a probe for investigating the chiral perturbation of the phenyl ring in these copolymers.

Indeed the tail of the strong CD longest wavelength band of the ester chromophore of MtA units can partially overlap the longest wavelength band (1L_b) of the phenyl group.

For a more accurate quantitative evaluation therefore the values of ellipticity between 250 and 280 nm have been corrected(15) by subtracting at every λ the dichroic absorption of the corresponding homopolymers mixture. In the copolymers the ellipticity of the 1L_b band, and then the dissymmetric perturbation of styrene units, increases with increasing the content, and then the average sequence length (\bar{l}_{MtA}), of the chiral co-units, reaching an asymptotic value for a molar content of MtA units larger than 70% ($\bar{l}_{\text{MtA}} = 4-5$)(Fig. 4).

This result is consistent with that observed in case of isotactic copolymers of optically active α -olefins and styrene(19) and can be very probably associated with a cooperative conformational effect. The value of the ellipticity at the saturation is comparable to that of the Ziegler-Natta catalyzed poly[(S)-5-methyl-1-heptene-co-St]s where the side chain

asymmetric carbon atom is also in γ position with respect to the main chain.

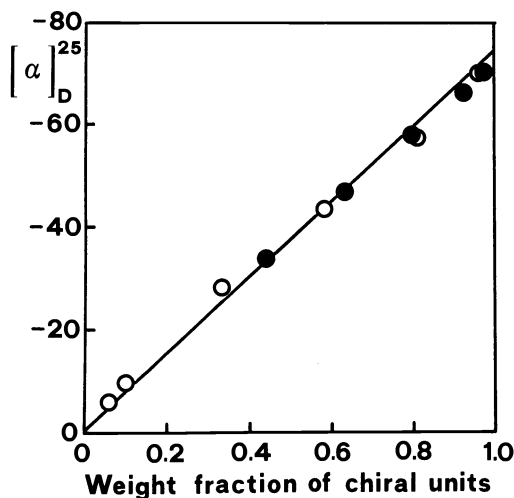
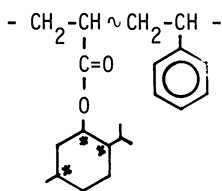
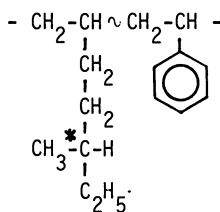


Fig. 1. Dependence of specific rotatory power in chloroform of copolymers from (-)-menthyl acrylate with styrene (●) or 1-vinylnaphthalene (○).



poly(MtA-co-St)



poly(5MH-co-St)

Moreover the ellipticity in poly(MtA-co-St)s is higher at any composition than in the low molecular weight structural model compounds (-)-menthyl 4-phenylbutyrate and (-)-dimenthyl 4-phenylheptandionate. This last has $\Delta\epsilon = -0.018$, whereas the corresponding poly(MtA-co-St) containing 34.7 mole-% of St, and then two menthyl groups per phenyl ring, exhibits a molar ellipticity value of + 0.062 per St unit(15).

A further confirmation of the conformational cooperative effect derives from the lower ellipticity of the alternating copolymer with respect to that of the random copolymer with low content of St units, the local surroundings of the phenyl chromophore being the same as in both copolymers the St units are substantially isolated.

Finally the dichroic absorption band of 1L_b electronic transition of phenyl chromophore has been observed to be very sensitive to structural effects as shown by the opposite sign of ellipticity in the alternating copolymers of St with MtA and MtMA(15).

In order to test the influence of chromophore structure on the "induced CD", these studies have been extended to copolymers of MtA or MtMA with vinylaromatic monomers containing condensed nuclei such as 1VN and 6VC. An appreciable increase of the ellipticity of the $\pi \rightarrow \pi^*$ electronic transitions has been indeed observed when going from St to 1VN for coisotactic copolymers with optically active α -olefins(13,20).

Copolymers of MtA with 1VN, prepared by radical initiation, show dichroic bands in the region of 1L_a electronic transition of the naphthalene chromophore, the ellipticity again increasing with an increase of MtA units content(16). The maximum dichroic absorption ($\Delta\epsilon$) was observed when practically all 1VN units were isolated between relatively long blocks of MtA units, the alternating copolymer displaying a lower $\Delta\epsilon$ as observed for the corresponding St copolymers. Fluorescence measurements show that energy migration occurs along the polymer chain depending on the composition and distribution of monomeric units, as such migration is very sensitive

to naphthalene-naphthalene side chain chromophores interactions.

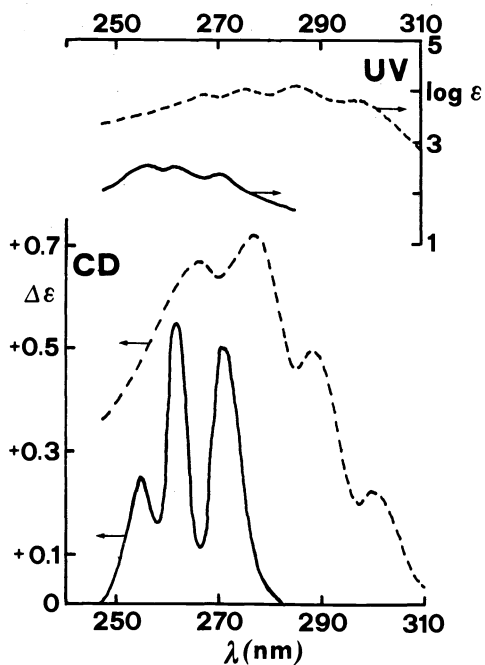


Fig. 2. UV and CD curves for copolymers of (-)-menthyl acrylate with styrene (—) or 1-vinylnaphthalene (----) containing about 5 mole-% of aromatic units (CD values for the St copolymers are multiplied by 5).

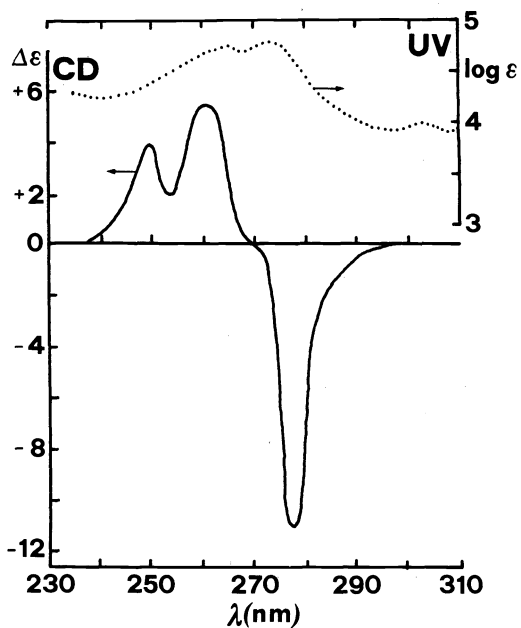


Fig. 3. UV (....) and CD (—) spectra of a (-)-menthyl acrylate/6-vinylchrysene(6VC) copolymer containing 44.5 mole-% of 6VC units.

In this connection fluorescence data are very useful to correlate CD spectra and sequence distribution. Dichroic bands in the region of the lowest energy electronic transition of π -electrons are also observed in the CD spectra between 240 and 350 nm for the copolymers of 6-vinylchrysene with MtA or MtMA(17). The strong dichroic absorption per aromatic unit, $\Delta\epsilon$ -15 \pm +5 in copolymers containing about 40% of VC, indicates that the nature of the chromophore is very important for the absolute value of the induced CD.

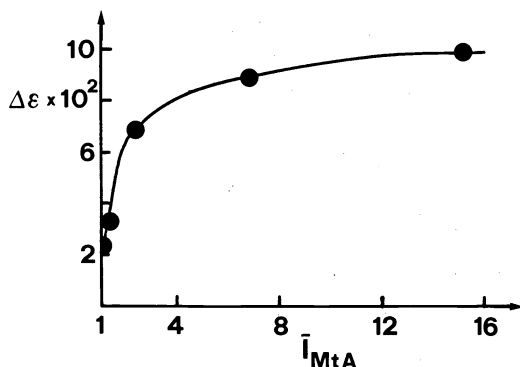


Fig. 4. Differential molar dichroic absorption coefficient at 262 nm versus mean sequence length of MtA units (\bar{l}_{MtA}) in the radically prepared poly(MtA-co-St)s.

POLYMERS CONTAINING THE CARBAZOLE CHROMOPHORE

These polymers (Table) deserve a separate section because of the large amount of work done and the unique features of carbazole chromophore which on the other side allow combining CD and fluorescence for structural investigation in a very definite way.

In this case investigations have been extended to the relationships between CD of carbazole containing units and type of comonomer and copolymer initiation process, sequence length distribution, distance of the carbazole chromophore from main chain. CD studies have been paralleled by UV absorption and fluorescence emission data which apart from their intrinsic interest can be conveniently used for evaluating comonomers distribution as for analogous copolymers of 1-vinylnaphthalene(16).

The most investigated monomer containing the carbazole chromophore is N-vinylcarbazole (NVC) which by virtue of its electronic structure can be polymerized by different initiators and can therefore be copolymerized with different optically active monomers thus allowing to obtain systems with markedly different primary structure.

Copolymers of NVC with (-)menthylvinylether(MtVE) prepared by $AlEtCl_2$ in CH_2Cl_2 at $-78^\circ C$ (21) and containing 99.0 down to 9.1 mole-% MtVE units show appreciable dichroic bands above 250 nm (Fig. 5), in a spectral region where the homopolymer of MtVE does not show any absorption (22). These dichroic bands centered at 258, 265, and 345 nm must therefore be associated with the lowest energy transitions of carbazole chromophore which become optically active thanks to the inclusion in copolymer macromolecules with MtVE. The molar dichroic absorption coefficient($\Delta\epsilon$) and its integrated value ($I = \int \Delta\epsilon d\nu$) increase with increasing content of optically active monomer units up to 80% and then decrease (Fig. 6)

This suggests that, contrarily to what was observed with styrene/MtA radical copolymers, the main contribution to CD of the aromatic chromophore is not merely due to isolated units in blocks of units derived from the optically active comonomer but also short blocks can give rise to strong CD bands. The existence of such species has been detected mainly from fluorescence spectra(23). Strong CD bands from interactions between chromophores of different units imply an ordered dissymmetric conformation of the macromolecules(helix) (24,25) which is compatible with a substantially coisotactic structure of the copolymer macromolecules. It is of interest to mention that the largest absolute values of $\Delta\epsilon$ are very close to those observed for homopolymers from (S)-9-(2-methylbutyl)-2-vinylcarbazole (26).

Similar behaviour is found for free radical copolymers of NVC with MtA and MtMA, which show in the 250-350 nm spectral region dichroic bands associated with $\pi \rightarrow \pi^*$ electronic transitions

of NVC chromophore(27).

TABLE. Optically active copolymers containing the carbazole chromophore

Optically active monomer	Non-chiral carbazole containing monomer	Polymerization initiator	Ref.
$\text{CH}_2 = \text{CH}-\text{O}$ 		$\text{AlEtCl}_2^{\text{a)}$	21,23
$\text{CH}_2 = \text{C}(\text{R})-\text{C}=\text{O}$ $\text{R} = \text{H}, \text{CH}_3$		AIBN ^{b)}	27
		AIBN ^{b)}	29
		AIBN ^{b)}	29
$\text{CH}_2 = \text{C}(\text{R})-\text{C}=\text{O}$ $\text{R} = \text{H}, \text{CH}_3$	 <i>para or meta</i>	AIBN ^{b)}	30

a) At -78°C b) At 60°C

Indeed in these copolymers stereoregularity could be fairly low, thus the maximum values for $\Delta\epsilon$ of copolymers containing 40 mole-% of NVC units are more difficult to explain. In any case at present no better explanation can be put forward than contributions to CD from interacting NVC units in a mutually dissymmetric disposition due to the secondary chain structure(25). Also a certain stereoregularity of these macromolecules cannot be excluded and NMR data could

clarify this point(28).

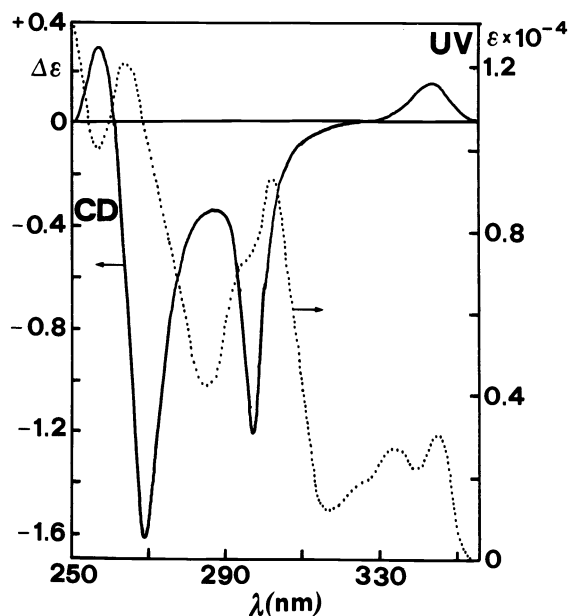


Fig. 5. CD(full line) and UV(dotted line) spectra in dichloromethane of a (-)-menthyl vinyl ether/9-vinylcarbazole(NVC) copolymer containing 16.7 mole-% of NVC units.

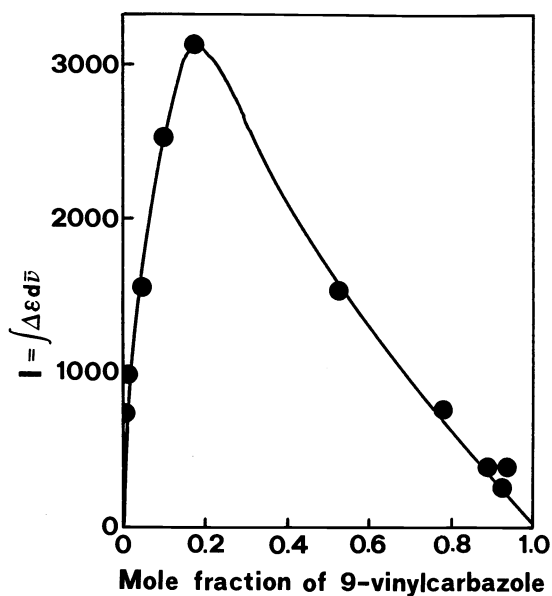


Fig. 6. Variation of the integrated dichroic absorption of the band at 265 nm with composition for (-)-menthyl vinyl ether/9-vinylcarbazole copolymers.

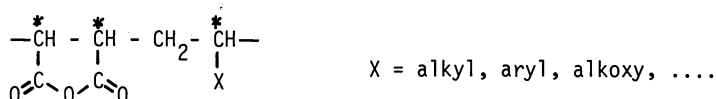
Substantially alternating copolymers of NVC with (-)-ethyl menthyl fumarate show again remarkable CD for the heteroaromatic chromophore comparable to that observed for the random copolymers

of NVC with MtVE, MtA and MtMA but appreciably higher than the low molecular weight model (-)menthyl-3-(9-carbazolyl) propionate(29). Slight deviation from this behaviour is observed for NVC/(-)dimethylfumarate copolymers containing more than 50 mole-% of the latter being too sterically hindered to allow formation of strictly alternating copolymers. In this last case a moderately larger CD is observed for copolymers containing 70 mole-% of NVC units. Also in these copolymers with substantially alternating structure dissymmetric interactions between NVC units cannot be excluded. The asymmetric broadening on the long wavelength side of the isolated carbazole chromophore fluorescence emission, the profile of the UV absorption spectra (maximum at 230 nm and a shoulder at 238 nm), ¹H-NMR spectra in the aromatic protons region (extra shoulder at 6.3 ppm) support the occurrence of interactions between remote carbazole groups responsible for excimer formation and contributing to the whole copolymer CD(29). The introduction of a spacer group between carbazole chromophore and main chain in copolymers of MtA or MtMA with 4- and 3-(9-carbazolylmethyl)styrene seems to eliminate this type of interaction, as NMR and fluorescence emission spectra are consistent with a "monomer type" behaviour(30). However even in this case appreciable dichroic bands are observed in the 240-350 nm region in spite of the large distance between chromophore and main chain. Around 240-260 nm the lowest energy $\pi \rightarrow \pi^*$ transition of the phenyl group can also give a CD contribution as observed in St/MtA or MtMA copolymers(14,15), however in that case the ellipticity would be considerably lower than the reported one thus indicating a prevalent contribution by the carbazole chromophore. It may be of interest to recall that in poly[(S)-4-sec.butylstyrene] the asymmetric carbon atom in the *para* position is not able to dissymmetrically perturb the main chain conformation(31). In the present case if, as it seems, no interactions between carbazole groups occur, the induced CD should be associated with a certain rigidity of the side chain allowing the transmission of the chiral perturbation by the menthyl groups. No spectroscopic evidence on the other hand exists of non bonded interactions with the ester group.

ALTERNATING COPOLYMERS

In the previous sections we have already discussed a few examples of alternating copolymers from vinylaromatic hydrocarbons or N-vinylcarbazole with optically active monomers. In those cases however the alternating copolymers were mainly investigated for comparison purposes with random copolymers.

In the present section the copolymers are considered of monomers which preferably give alternating products such as maleic anhydride (MAN), maleates and fumarates. These copolymers present the interesting aspect of a primary regular structure which is clearly not the case with random copolymers. Moreover they are also in principle useful for investigating phenomena of asymmetric induction during the polymerization process. Indeed the repeating units contains in the main chain three non equivalent asymmetric carbon atoms



and the prevalence of absolute configurations of a single type should bring to "induced optical activity" in the anhydride chromophore. If however the side chain contains asymmetric centers of a predominant configuration, that is $\text{CH}_2 = \text{CHX}$ is an optically active monomer, the induced optical activity can also arise from a dissymmetric conformational arrangement of the macromolecules as in the case of the previously discussed vinyl and acrylic copolymers. In these last indeed the main chain asymmetric carbon atoms cannot give an appreciable contribution to the polymer chiroptical properties(32). CD studies on the alternating copolymers, after removal of X, are very suitable to demonstrate the occurrence of asymmetric induction at the level of the main chain tertiary carbon atoms and thus the presence of stereoregularity in the copolymer(33). The main problem is clearly the real possibility of removing the X group completely; for a reliable successive checking by CD it is convenient that X contains a chromophore absorbing in a well distinct region with respect to maleic anhydride or ester units.

In order to gain information on the chiroptical properties of a "neat" anhydride chromophore in a copolymer with an optically active vinyl monomer, the copolymers of MAN with chiral olefins was very useful as the α -olefins units absorb well below 180 nm while the anhydride chromophore is centered at about 220-240 nm(34).

The copolymers of MAN with several α -olefins [(S)-4-methyl-1-hexene, (S)-5-methyl-1-heptene] and vinylidene olefins [(S)-2,4-dimethyl-1-hexene, (S)-2,5-dimethyl-1-heptene and (3S,9S)-

-3,9-dimethyl-6-methylenundecane show a molar rotatory power at sodium D-line at least one order of magnitude lower than the corresponding isotactic poly(α -olefins). This can be considered a first indication of low cooperative conformational effect but also of low stereoregularity. On the other side all the above copolymers show dichroic bands in the absorption region of the $n \rightarrow \pi^*$ electronic transition of the anhydride carbonyl chromophore (Fig. 7)

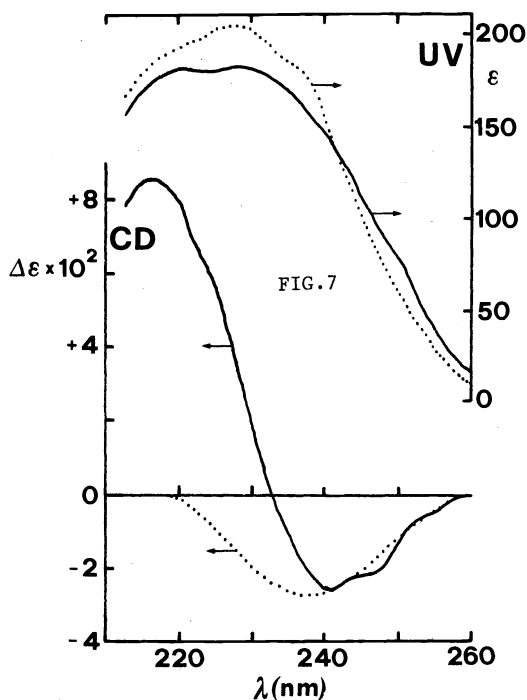


Fig. 7. UV and CD spectra of alternating copolymers of maleic anhydride with (S)-5-methyl-1-heptene (dotted lines) and with (3S,9S)-3,9-dimethyl-6-methylenundecane (full lines)

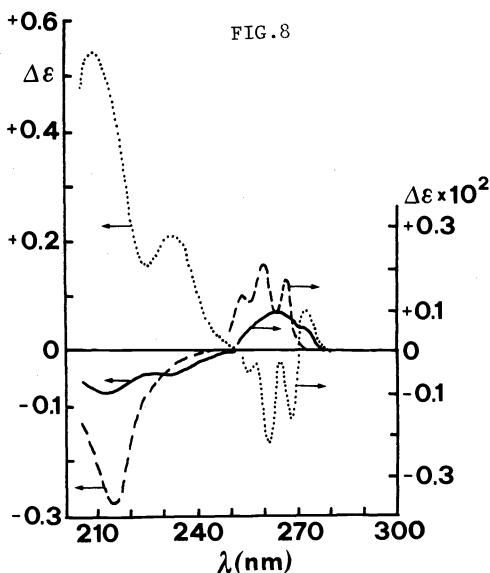
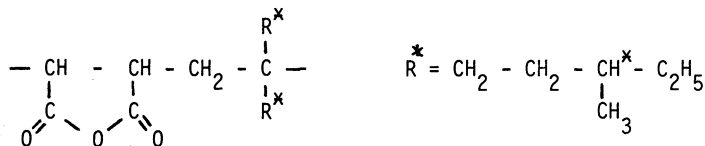


Fig. 8. CD spectra in THF at 25°C of poly[(S)- α -methylbenzyl methacrylate] (-----) and of (S)- α -methylbenzyl methacrylate (MBMA)/trityl methacrylate copolymers containing 20 (——) and 5 mole-% (.....) of MBMA counts.

When the starting olefin contains only one asymmetric carbon atom the copolymer ellipticity is relatively small, $\Delta\epsilon$ being 0.01 ± 0.03 per MAN residue, while an appreciable increase to +0.085 is observed with (3S,9S)-3,9-dimethyl-6-methylenundecane which possesses two asymmetric carbon atoms in the side chains. This result is a first indication that conformational effects are probably important, considering also that in this copolymer the olefin units have no asymmetric carbon atoms in the main chain (35).



Quite similar results have been obtained by CD investigation of alternating copolymers from MAN and optically active vinyl ethers structurally similar to the above α -olefins (36). In this case for the copolymers of MAN with vinyl ethers derived from secondary alcohols [(S)-2-butanol and (S)-2-octanol] the removal of the chiral alkyl group was attempted by HBr in benzene. However no more than 90% of the groups was removed, indicating the difficulty in this type of study and in the obtainement of reliable results for the copolymer chiroptical properties after cleavage of optically active groups.

Alternating copolymers of MAN, dimethylmaleate, and dimethylfumarate with (-)-menthylvinylether also show dichroic bands of rather low ellipticity ($\Delta\epsilon$ per monomeric unit 0.006 ± 0.033) in the 250-200 nm spectral region. These bands are practically disappearing after cleavage of

menthyl groups, a residual low optical activity being observed only for the MtVE/dimethylmaleate copolymer(37).

MtVE has been again used as optically active comonomer for the alternating copolymerization with styrene(St)(38), N-phenylmaleimide(NPMI)(38), vinylene carbonate(VCA)(39) and indene(IN)(39). The MtVE/St copolymer shows only a vanishingly small CD band around 260 nm, in the region of the lowest energy $\pi \rightarrow \pi^*$ electronic transition of the aromatic chromophore, which disappears completely after removing the menthyl groups. In case of NPMI the original alternating copolymer with MtVE has an appreciable ellipticity between 270 and 210 nm with maxima at 257 nm($\Delta\epsilon = + 0.07$) and at 220 nm($\Delta\epsilon = + 0.23$). These values drop to less than one half in the ether-cloven polymer(38). The copolymers of MtVE with both VCA and IN show extremely low CD at the limit of instrument sensitivity, thus indicating that these systems are less suitable than the other for this type of study(39).

In a different approach the optically active group has been introduced in the maleic acid derivative by using (-)menthyl hydrogen maleate(MtHMA) in copolymerization experiments with St and IN(40). The former copolymer shows a relatively strong CD band at 258 nm($\Delta\epsilon$ per monomeric unit = - 0.86) to be associated with the phenyl chromophore, thus indicating the occurrence of an asymmetric perturbation of the achiral comonomer. After removing the menthyl group by ester hydrolysis, no CD is observed above 250 nm indicating that the asymmetric perturbation of the phenyl group was predominantly of conformational origin, as proposed for MAN alternating copolymers with chiral vinyl ethers(36) or olefins(35). On the other side dichroic bands for the hydrolysed copolymers have been detected only below 250 nm, where also the carboxylate groups absorb. Indeed both hydrolysed copolymers show appreciable CD around 240-230 nm($\Delta\epsilon \sim 0.3$ per monomeric unit) which has been attributed to the $n \rightarrow \pi^*$ electronic transition of the carboxylic group arising from asymmetric induction at the level of the main chain asymmetric carbon atoms of the units derived from menthyl hydrogen maleate(40).

A part of the real meaning of these studies for demonstrating asymmetric induction by the optically active comonomer during the alternating copolymerization process, these results clearly indicate that CD is a powerful technique for approaching these type of mechanistic and structural studies. Indeed examination of CD curves in the absorbing region of the chromophores present in the achiral comonomer, before and after cleavage, can allow to determine possible asymmetric effects by the chiral side chains during the polymerization. Finally CD data indicate that the dissymmetric perturbation of the chain conformation in alternating copolymers seems to be relatively smaller than that produced by cooperative conformational effects in blocks of optically active units.

COPOLYMERS OF OPTICALLY ACTIVE AND AROMATIC ACRYLIC DERIVATIVES

The copolymerization of two comonomers having the same type of polymerizable double bond offers obvious synthetic advantages. Thus (S)- α -methylbenzyl methacrylate(MBMA) has been copolymerized with trityl methacrylate(TrMA) in the presence of *n*.BuLi at - 78°C and with THF as the solvent. The copolymers show remarkable optical activity dependence on composition, the rotatory power at the sodium D-line changing from negative to positive with increasing the content of TrMA units. In accordance the CD curves show a changing of sign of the dichroic band at 260 nm, connected with 1L_b electronic transition of the π -electrons of the aromatic chromophore, and also of the systems of dichroic bands between 250 and 200 nm, where both the 1L_a band of the aromatic chromophore and the $n \rightarrow \pi^*$ electronic transition of the carbonyl in the ester groups are located(Fig. 8)(41). NMR analysis indicates that the isotacticity degree increases with TrMA content probably because bulky trityl groups prevent the syndiotactic placement even in THF. These results can be nicely explained by assuming that the isotactic sequences of TrMA units assume a single screw sense helical conformation. It is of interest to note that the maximum value of ellipticity is obtained with only 5 mole-% of MBMA units in the copolymer, indicating that the TrMA units helix is maintained by the cooperative steric interactions among trityl groups, only a small amount of optically active comonomer being sufficient to induce a single screw sense(Fig. 8). It has been also shown that the positive rotatory power decreases with time and temperature reaching a stationary value, probably due to the equilibrium between right- and left-handed helical sections. The position of the equilibrium depends on the average length of sequences of TrMA units(42). This copolymer provides a clear example that CD can be conveniently used also when both comonomers contain the same chromophores, provided structural changes produced by different composition are remarkable. An interesting achiral acrylic ester is methyl α -phenylacrylate(MPhA) as it contains in addition to the acrylic reactivity also the aromatic chromophore directly bound to the double

bond and then to the main chain in the polymer.

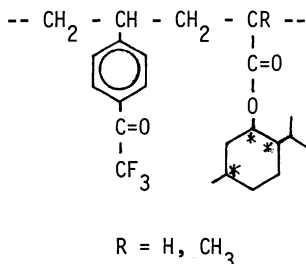
MPhA has been copolymerized with (S)- α -methylbenzyl methacrylate (MBMA) by *n*.BuLi in toluene at different temperatures(43). The presence of the same chromophoric moieties in both monomers hindered a thorough CD investigation. In any case only the CD spectrum of the alternating copolymer obtained at 30°C has been reported. This shows exactly the same shape as the homopolymer of MBMA, but the ellipticity at any wavelength is less than one half(43).

More information can be obtained from the copolymers of MPhA with (-)-menthyl acrylate or methacrylate, as the two optically active comonomers do not contain any aromatic chromophore(44). These copolymers show an appreciable CD in the absorption region of the 1L_b band of the phenyl chromophore which is opposite in sign to that observed for the corresponding styrene copolymers. This clearly indicates on one side the occurrence of dissymmetric perturbation of achiral units, but also that the sign of the dichroic band depends appreciably on the structure of the achiral comonomer and not simply on the conformational dissymmetry produced by the chiral comonomer(44).

POSSIBLE APPLICATIONS AND CONCLUDING REMARKS

The data reported in the previous sections suffice in our opinion to show the type of information which is possible to gain from the CD analysis of optically active copolymers and the cases to which this analysis can be successfully applied. In addition to sophisticated stereochemical insights, the copolymerization between an optically active monomer and an achiral comonomer can provide an economic method for the synthesis of dissymmetric materials with particular structure and steric requirements.

In the former case it is particularly important that the chromophore to be analyzed by CD gives rise to strong dichroic effects sensitive to even subtle stereochemical changes. Largely polarizable groups are in general more convenient, sometimes aided by the presence of heteroatoms. In addition to the already reported examples it is worthwhile to mention at this point the copolymers of MtA and MtMA with *p*-vinyltrifluoroacetophenone (VTFA) giving in the absorption region of the π -electrons system of the acetophenone chromophore two dichroic bands, a positive one at 280 nm and a second negative at 258 nm, $\Delta\epsilon$ per VTFA unit being $+0.75 \pm 0.80$ and -0.5 ± 0.8 with only 40 mole-% of units from the optically active comonomer(45). Certainly in this case a contribution to the CD from exciton coupling between side chains cannot be excluded and the examination of copolymers with a low content of VTFA units would be desirable.



If the achiral monomer of interest does not contain suitable chromophores, this can be present in the optically active comonomer as in the case of (S)-4-phenyl-1-hexene used to study the conformation in solution of poly(4-methyl-1-pentene)(46).

The most obvious application of functional optically active copolymers is as chiral reagents for asymmetric chemical reactions involving chiral or prochiral substrates. Thus copolymers of optically active α -olefins with phosphinated styrene have been used as optically active ligands for transition metal complexes(47). Moreover copolymers of MtA or MtMA with 4-vinylpyridine or *p*-dimethylaminostyrene, as such or in form of quaternary ammonium salts, have been used for heterophase catalysis(48).

Finally the introduction in optically active copolymers of photochromic side chains, such as azobenzene or stilbene(49), can supply synthetic materials where structural changes can be produced by light irradiation and detected by CD-analysis as shown in case of polypeptides(50).

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