Poly(methacrylic acid) Derivatives. 7. Chiroptical Properties of Optically Active Poly(*N*-methacryloyl-L-alanine) and Poly(*N*-methacryloyl-L-alanine-*co*-*N*-phenylmethacrylamide)

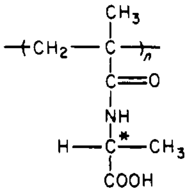
Joelle Morcellet-Sauvage, Michel Morcellet,* and Claude Loucheux

Laboratoire de Chimie Macromoleculaire, ERA No. 827 du CNRS, Université des Sciences et Techniques de Lille, 59655 Villeneuve d'Ascq Cedex, France. *Received March 30, 1983*

ABSTRACT: UV, ORD, and CD spectra of poly(*N*-methacryloyl-L-alanine) (PNMA), *N*-isobutyroyl-L-alanine (NIBA), and random copolymers of chiral *N*-methacryloyl-L-alanine and achiral *N*-phenylmethacrylamide units were investigated in different solvents, especially water and methanol. CD spectra of PNMA and of its model molecule, NIBA, were found to be very similar and were explained by the contributions of the electronic transitions of the amide and carboxyl chromophores in the accessible wavelength range, excluding any appreciable contribution arising from the conformation of the polymer. For the copolymers, three additional electronic transitions relative to the aromatic chromophore of the achiral unit were found to display induced optical activity due to the neighboring chiral residue which, in turn, is perturbed by the presence of the aromatic chromophore. Nonlinear variations of the chiroptical properties (molar rotation and molar ellipicity) were explained by this induced optical activity in the absence of ordered conformation.

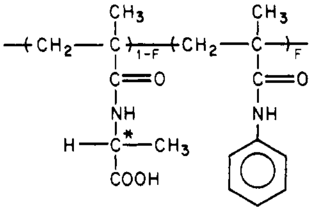
Introduction

We have previously reported[1] the synthesis and characterization of poly(*N*-methacryloyl-L-alanine) (PNMA) (I) and of a series of poly(*N*-methacryloyl-L-alanine-*co*-*N*-phenylmethacrylamide) polymers (II). The conformational behavior of these polymers has been studied by UV spectroscopy,[2] potentiometric and conductometric[3] titrations, and viscosimetric[4] and microcalorimetric techniques.[5]



$$-\!\!\left(\text{CH}_2-\text{C}(\text{CH}_3)(\text{C}{=}\text{O}\,\text{NH}-\overset{*}{\text{C}}\text{H}(\text{CH}_3)\text{COOH})\right)\!\!-_n$$

I, PNMA



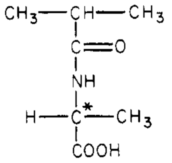
II, P_F

According to the mechanism of their synthesis by free radical polymerization, both polymer I and polymer II were considered to be mainly atactic and therefore unable to adopt any kind of regular conformation in solution, as it is the case for stereoregular poly(α-olefins), for example.[6] In addition, the determination of the reactivity ratios for the synthesis of polymer II[7] indicates that there are no long sequences of the *N*-methacryloyl-L-alanine and *N*-phenylmethacrylamide residues that are randomly distributed along the main chain.

Polymer I is readily soluble in water, where it takes a random coiled conformation. When the molar fraction F of hydrophobic units is less than 0.5, polymer II is soluble in water, where it takes either a random coil conformation or a so called compact conformation when F is higher than 0.14. Both polymers are soluble in methanol, where their conformation is a random coil.[1]

When dealing with stereoirregular macromolecules, one may generally explain the chiroptical properties by taking into account local effects of solvent, ionization, and salt, for example, on the isolated chromophores, excluding the contribution of any ordered secondary structure.[8,9] The comparison with the chiroptical properties of a small molecule taken as a model for the repeat unit of the polymer is often useful and allows one to distinguish contributions due to a possible macromolecular effect.[10]

In the present study, we investigated the chiroptical properties of polymers I and II by UV, ORD, and CD spectroscopy. CD spectra were compared with those of a model compound, *N*-isobutyroyl-L-alanine (III).



$$\text{CH}_3-\text{CH}(\text{CH}_3)-\text{C}{=}\text{O}-\text{NH}-\overset{*}{\text{C}}\text{H}(\text{CH}_3)-\text{COOH}$$

III, NIBA

As polymer II is a random copolymer of chiral and achiral units, we also examined the possibility of optical activity induced in the achiral unit by the chiral center. The existence of an induced optical activity for an achiral unit has been suggested[11] and demonstrated[12,13] for random stereoirregular copolymers of acrylic acid and *N*-*sec*-butyl-*N*-methacrylamide. In this case, the dichroic band due to the induced optical activity in the COOH chromophore is masked by the intense dichroic bands arising from the amide chromophores. The asymmetric perturbation of the carboxyl chromophore has been more easily demonstrated with copolymers of acrylic acid and optically active alkyl vinyl ethers because of the transparency of the ether unit in the 200–220-nm wavelength range.[14,15]

In our case, it was expected that a possible induced optical activity would be easily demonstrated since some of the electronic transitions of the *N*-phenylmethacrylamide unit are located in a wavelength domain where no other chromophore absorbs.

Experimental Section

Samples. *N*-Methacryloyl-L-alanine was prepared from methacryloyl chloride and L-alanine (optical purity 99%) according to the method of Kulkarni and Morawetz[16] (mp 130 °C; $[\alpha]^{20}{}_{546}$ $-41°$ in water).

N-Phenylmethacrylamide was obtained by reaction of methacryloyl chloride with aniline in benzene[17] (mp 85 °C).

The model molecule, *N*-isobutyroyl-L-alanine (NIBA) (III), was prepared from isobutyroyl chloride and L-alanine in the same way as *N*-methacryloyl-L-alanine.

Polymers I and II were obtained from *N*-methacryloyl-L-alanine and *N*-phenylmethacrylamide by radical polymerization or copolymerization in dioxane initiated by AIBN.[1] Poly(*N*-methacryloyl-L-alanine), polymer I ($[\alpha]_{546}{}^{20}$ $-42°$ in water), will be referred to thereafter as PNMA.

Copolymers II will be named as P_F, F being the mole fraction of the *N*-phenylmethacryalmide residue.

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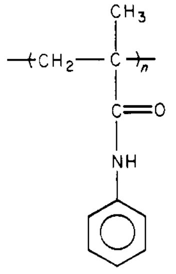
Table I
UV Data for the Different Samples in Water and Methanol

	water		methanol	
	λ_{max}	ϵ_{max}	λ_{max}	ϵ_{max}
NIBA	187	7900	192	9400
PNMA	190	5300	193	4300
P50	197	11400	199	13850
	240[a]	4060	242[a]	6500
PNPMA	insoluble		200	20200
			242	13000
acetanilide	insoluble		200	33800
			242	13000

[a] All copolymers from P14 to P50 in water and from P14 to P82 in methanol present absorption bands at the same wavelengths, with ϵ values depending on their composition.

Poly(*N*-phenylmethacrylamide) (PNPMA (IV)) was obtained by radical polymerization of *N*-phenylmethacrylamide in dimethyl sulfoxide. This sample is the only one that is optically inactive.



IV, PNPMA

All small molecules and polymers were also identified by acid–base titration and by UV, IR, and NMR spectroscopy. Solvents used for UV, CD, and ORD measurements were spectrograde quality.

Methods. UV spectra were recorded at room temperature with a Cary 118 spectrometer flushed with dry nitrogen. The molar extinction coefficient ϵ is expressed in L·mol^{-1}·cm^{-1}.

ORD data were obtained at room temperature with a Perkin-Elmer MC 141 polarimeter in the range 300–600 nm. The molar rotatory power $[m]$ is expressed in deg·cm^2·dmol^{-1}.

CD spectra were recorded at room temperature with a Jobin-Yvon Mark III dichrograph flushed with dry nitrogen. The molar ellipticity $[\theta]$ is given in deg·cm^2·dmol^{-1}. For copolymers, the values of $[m]$ or $[\theta]$ are calculated by using the mean molecular weight M_r of a repeat unit.

Results and Discussion

UV Spectra. UV spectra were recorded in water, methanol, 2-chloroethanol (CE), dioxane, and trifluoroethanol (TFE).

NIBA and PNMA show only one absorption band around 190 nm in water and methanol (Table I). The maximum was not observed in dioxane, CE, and TFE because of the absorption of the solvent. Though the 190-nm band seems simple, it actually results from many electronic transitions arising from the amide and carboxyl chromophores, as will be shown later by comparison with the CD spectra. This band is slightly red-shifted when going from NIBA to PNMA.

All the copolymers show two absorption bands: the first one, located near 197–200 nm, is red-shifted when compared to PNMA. This is due to the additional contribution of the aromatic amide chromophore, which absorbs at 200 nm (see PNPMA). Its ϵ value increases with F, the amount of *N*-phenylmethacrylamide residue. The second band, due to the aromatic chromophore, is observed at 242 nm and its molar extinction coefficient increases linearly with F.[1]

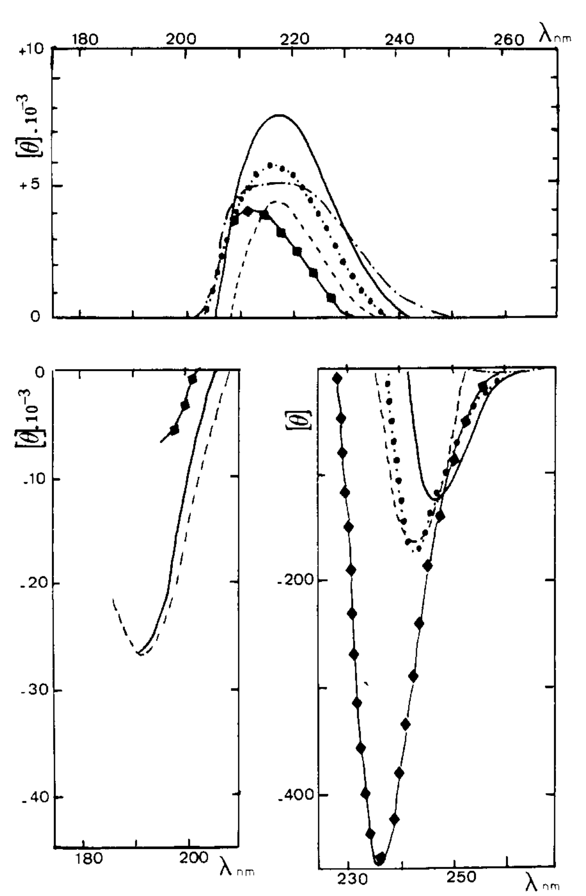


Figure 1. CD spectra of NIBA in methanol (—), 2-chloroethanol (●), dioxane (-·-), water (---), and trifluoroethanol (♦) at room temperature.

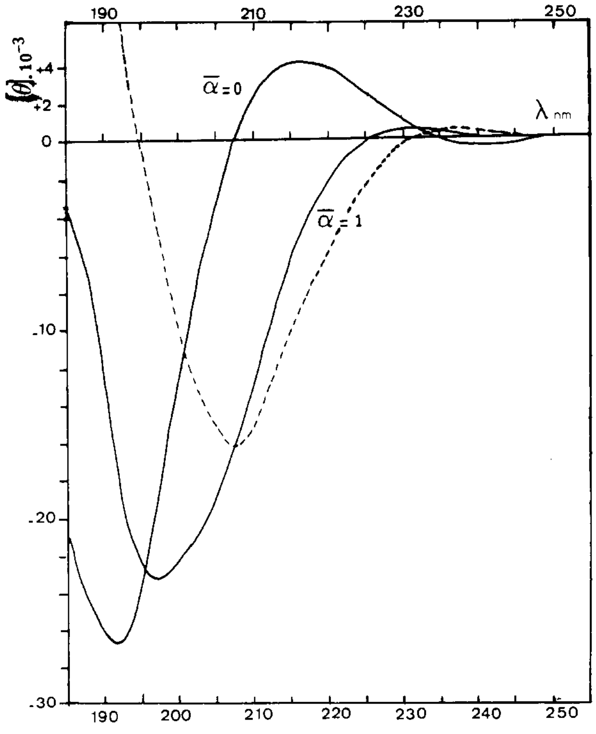


Figure 2. Effect of ionization on the CD spectrum of NIBA in water ($\bar{\alpha}$ = 0, $\bar{\alpha}$ = 1 (—); $\Delta[\theta] = [\theta]_{\bar{\alpha}=1} - [\theta]_{\bar{\alpha}=0}$ (---)).

CD Spectra of NIBA and PNMA. CD spectra of NIBA between 185 and 300 nm in different solvents are presented in Figure 1. They all consist of three bands, the position and intensity of which depend more or less on the polarity of the solvent. First, a weak negative band

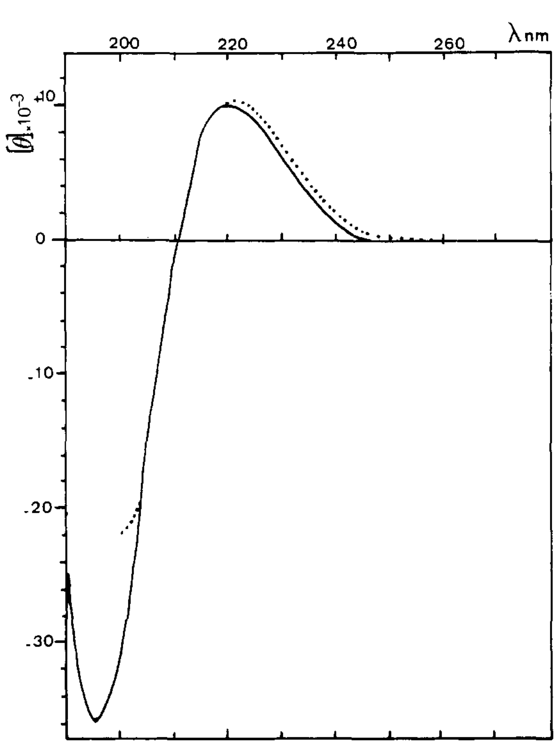


Figure 3. CD spectra of PNMA in methanol (—) and 2-chloroethanol (···) at room temperature.

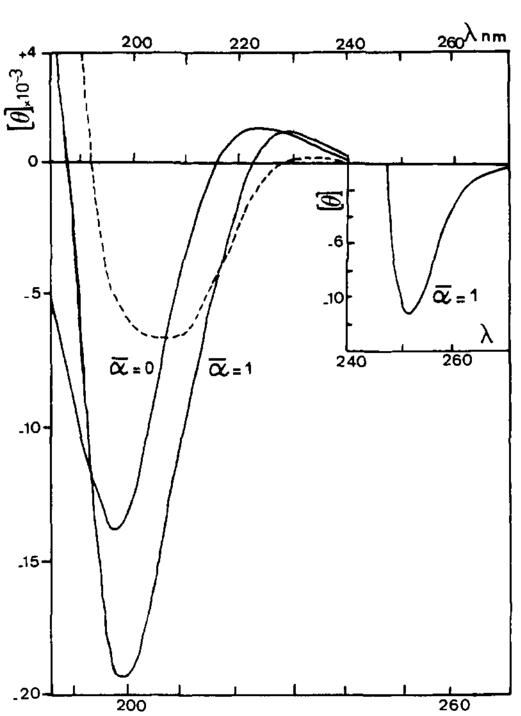


Figure 4. Effect of ionization on the CD spectrum of PNMA in water ($\bar{\alpha}$ = 0, $\bar{\alpha}$ = 1 (—); $\Delta[\theta] = [\theta]_{\bar{\alpha}=1} - [\theta]_{\bar{\alpha}=0}$ (---)).

appears around 240 nm (except in dioxane, where a very slight band seems to appear near 260 nm). When the polarity of the solvent is increased, the intensity of the band increases strongly and it is blue-shifted down to 236 nm in TFE. Taking into account its low rotational strength and its marked sensitivity to the solvent, one may attribute this band to the n → π* transition of the amide chromophore.[18,19]

A second dichroic band, positive, the intensity of which ranges from +4000 to +7700 deg·cm^2·dmol^{-1} depending on the solvent, appears near 216 nm. In water, this band is very sensitive to ionization, which induces a red shift of about 15 nm and a decrease of the intensity (Figure 2). In Figure 2 is also shown the difference spectrum of NIBA at $\bar{\alpha}$ = 1 and $\bar{\alpha}$ = 0, where it appears that the effect of ionization is maximum at λ = 207 nn. This wavelength is generally attributed to the n → π* transition of the carboxyl chromophore.[13-15,19,20] (According to Listowsky et al., the sign of the CD band associated with the n → π* transition of the COOH chromphore is often inverted upon ionization.[21] As this band is usually rather weak ($|[\theta]|$ = 100–1000 deg·cm^2·dmol^{-1}),[13-15] another contribution must be expected around 216 nm, which is very probably the $\pi_1 \rightarrow \pi^*$ transition of the amide chromophore.[22] The dichroic band resulting from these two transitions is only slightly sensitive to the nature of the solvent since the increase of polarity has opposite effects on the two transitions.

A third intense, negative, band is found at 192 nm in water and methanol. This band, which determines the location of the maximum in UV absorption, changes only slightly upon ionization. For this reason, it cannot be attributed to the π → π* transition of the carboxyl chromophore, which, in addition, is usually located below the absorption limit of the solvent, near 172 nm.[19] This band may tentatively be assigned to the $\pi_2 \rightarrow \pi^*$ transition or the n → σ* transition of the amide group, the latter being located close to 200 nm according to Urry.[23]

The CD spectra of PNMA present essentially the same features as those of NIBA (Figures 3 and 4). In methanol, water, and CE, the dichroic bands observed near 220 and 200 nm are red shifted compared to those of NIBA (Δλ = +5–8 nm). This shift, which could be related to an increased steric hindrance around the amide chromophore due to the macromolecular chain,[22] is also observed in the UV spectra (Table I). In water, the 200- and 220-nm bands are twofold less intense than for NIBA, whereas the n → π* amide Cotton effect gives rise to a very slight band that is within the sensitivity limit of the dichrograph. The effect of ionization is weaker than for NIBA and it is also at a maximum near 207 nm, corresponding to the n → π* Cotton effect of the carboxyl chromophore. The CD spectrum of ionized PNMA suggests the presence of an intense positive band below 185 nm, which could be attributed to the π → π* transition of COOH and/or to the inaccessible transitions of the amide chromophore perturbed by the ionization of the carboxyl group.

In methanol and CE, no dichroic band is observed near 240 nm. This probably results, in part, from the weakening of the n → π* amide Cotton effect compared to that of NIBA, as in water, but mainly from the increase of the intensity of the 220-nm band, which is also slightly red shifted. In these two solvents, the 220-nm band has approximately the same intensity as for NIBA.

The intensity of the 220-nm band of PNMA is 8 times greater in methanol than in water, which explains why the molar rotation in the visible range (350–600 nm) is approximately 4 times less negative in methanol than in water (Figure 5).

That the dichroic spectra of PNMA in water, methanol, and CE are very similar to those of the model molecule NIBA clearly demonstrates that no appreciable contribution of the macromolecular conformation has to be considered for this stereoirregular polymer. Therefore, its chiroptical properties depend essentially on local effects such as solvation, ionization, steric hindrance, etc.

Optical Activity of the Copolymers. Figure 5 shows ORD spectra of PNMA and some of the copolymers in water and methanol. All the spectra are normal and complex and present the same features even though the conformations of the copolymers (such as P50) are dif-

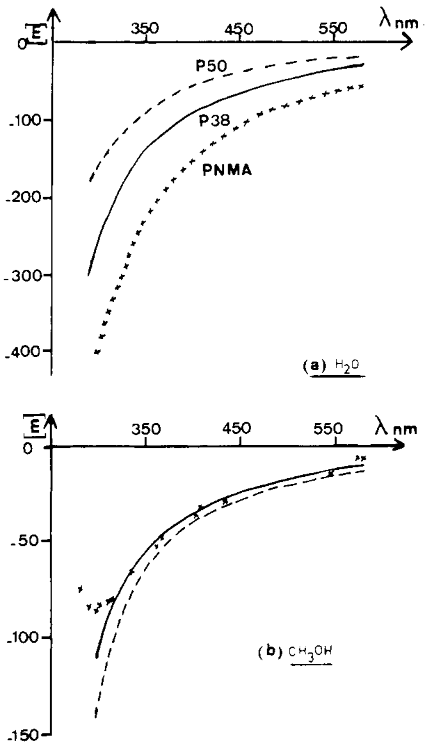


Figure 5. ORD spectra of PNMA (×), P38 (—), and P50 (- -) in water (a) and methanol (b).

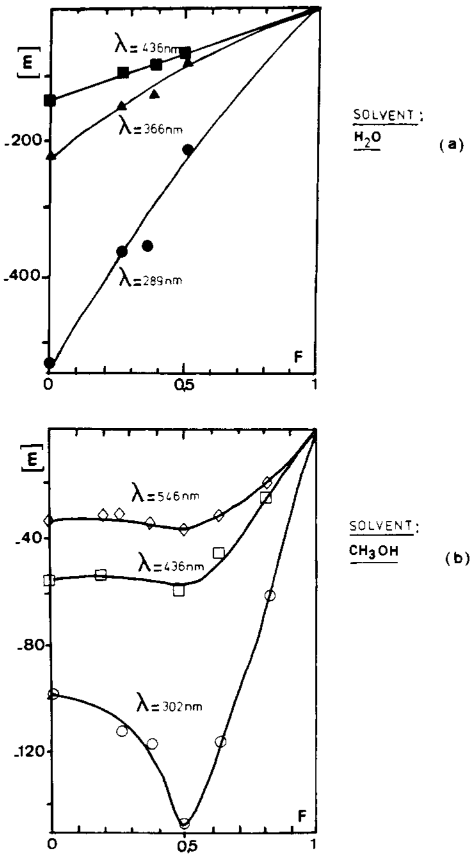


Figure 6. Composition dependence of the molar rotation [*m*] at different wavelengths in water (a) and methanol (b).

ferent in water and methanol.[1,3] Figure 6 gives the variation of the molar rotation as a function of the mole fraction F of the N-phenylmethacrylamide residue at different wavelengths. In water, [*m*] varies linearly with *F*, whatever the wavelength. Thus, the molar rotation of the copolymers is a linear combination of the optical activity of the two kinds of residues. In methanol, on the other hand, the variation of the molar rotation is not linear: the deviation from linearity is a maximum for *F* = 0.5 and increases when λ decreases.

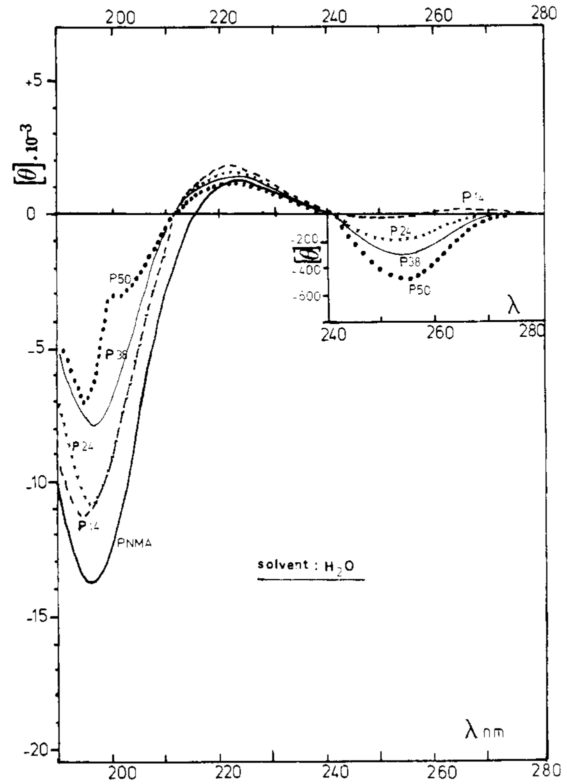


Figure 7. CD spectra of PNMA, P14, P24, P38, and P50 in water.

For copolymers having more or less ordered conformations, the nonlinear variations of chiroptical properties have been explained by conformational effects in the main chain or in the side chains.[24-26] When nonlinear variations of the chiroptical properties are observed in the absence of conformational order, the interaction of the chromophores with the immediate neighboring residues and/or optical activity induced in the achiral chromophores is invoked.[13,15] In our case, the copolymers take no ordered structure in methanol.[1] Therefore, the results of Figure 6 suggest the existence of an induced optical activity in the UV range.

This appears clearly in Figures 7 and 8, which show the CD spectra of PNMA and the copolymers in water and methanol. Apart from the two bands near 195 and 220 nm, already observed for PNMA, the intensity of which depends on the composition of the copolymers, a new band appears near 255 nm in the two solvents. Its intensity increases with the proportion of achiral units up to *F* = 0.52 (limit of solubility) in water. In methanol, it increases up to *F* = 0.63 and then decreases.

In water (Figure 7) the intensity of the 220-nm band does not change very much whereas that of the 195-nm band strongly decreases, which explains why the molar rotation becomes less negative in the visible range when *F* increases (Figure 5). In the same way, the constancy of [*m*] in methanol when *F* increases (Figure 5) may be explained by the simultaneous decreases of the positive and negative bands at 220 and 195 nm (Figure 8).

The negative CD band near 255 nm is about 2 times more intense in methanol than in water (Figures 7 and 8). Thus the perturbation brought about by this additional Cotton effect in the visible range is more important in methanol, especially as the molar rotation due to other contributions is already 5 times lower in this solvent than

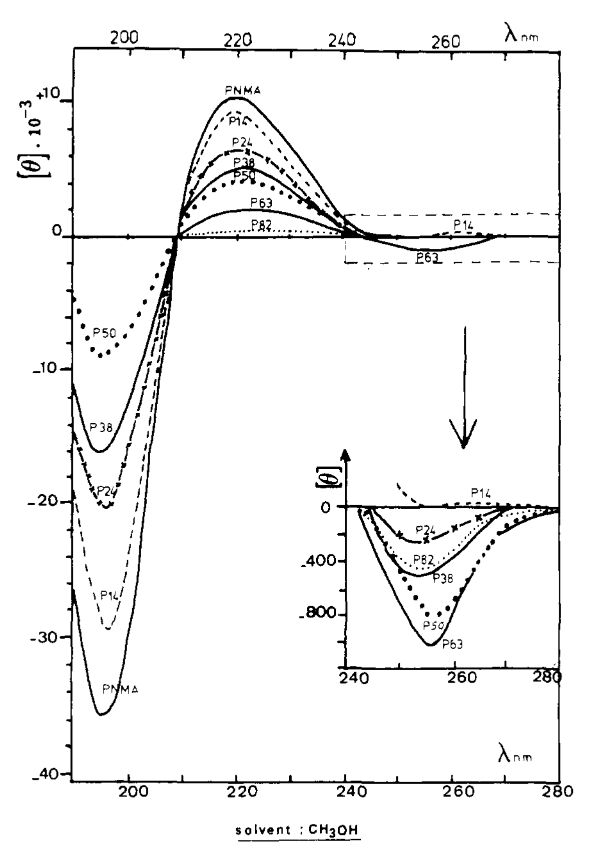


Figure 8. CD spectra of PNMA, P14, P24, P38, P50, P63, and P82 in methanol.

in water. This explains the difference between the two sets of curves in Figure 6.

The way in which the intensity of the 220-nm band varies when F increases and the appearance of a shoulder in the dichroic spectrum of P50 in water (Figure 7) suggest the existence of optically active transitions of the achiral residue below 240 nm. It is thus necessary to examine in detail the expected electronic transitions of the aromatic unit in the far-UV range. Three $\pi \rightarrow \pi^*$ electronic transitions are known for aromatic compounds over 175 nm.[20,27] For benzene in water, one observes two allowed transitions giving rise to two strong absorption bands, at 184 nm (^1B) and the so-called primary band at 203.5 nm (^1L_A). In addition, a forbidden transition (^1L_B) corresponding to a secondary band with a weak intensity is centered near 254 nm. When the benzene ring is substituted, these bands are red shifted, especially when the substituent contains a nitrogen, oxygen, or sulfur atom; in addition, the intensity of the secondary band (^1L_B) increases.[20] For acetanilide, which can be considered as a model molecule for the N-phenylmethacrylamide residue, the ^1L_A band is found at 238 nm (ϵ = 10 500 L·mol^{-1}·cm^{-1}) and the ^1L_B band appears as a shoulder around 280 nm in water.[28] When the polarity of the solvent is increased, the ^1L_A transition is red shifted, whereas the ^1L_B is usually blue shifted.[28,29]

In the dichroic spectra, the forbidden ^1L_B transition gives a weak band around 260–290 nm ($[\theta]$ = 50–200 deg·cm^2·dmol^{-1}),[30–32] the rotational strength of which strongly increases when the aromatic chromophore is involved in an ordered conformation.[33] The ^1L_A transition is about 10 times more intense than the ^1L_B transition and 10 times less intense than the ^1B transition near 190 nm,[34] which, in addition, may exhibit an exciton splitting when an ordered conformation exists.[33]

Assuming first that the electronic transitions of the amide and carboxyl chromophores of the chiral units are not appreciably perturbed by the presence of the aromatic chromophore of the achiral unit, the induced optical activity may be calculated by

$$\Delta[\theta]_{\lambda,F} = [[\theta]_{\lambda,P_F} - [\theta]_{\lambda,\mathrm{PNMA}}](1 - F) \qquad (1)$$

where $[\theta]_{\lambda,P_F}$ and $[\theta]_{\lambda,\mathrm{PNMA}}$ are the molar ellipticities of a copolymer and of PNMA at a given wavelength λ. Figures

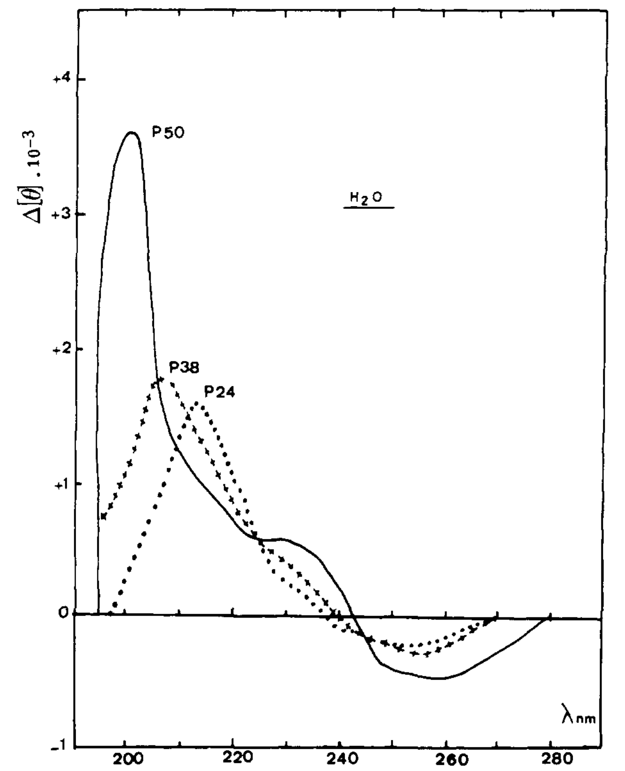


Figure 9. Difference CD spectra Δ[θ] = $f(\lambda)$ for the different copolymers in water (see text).

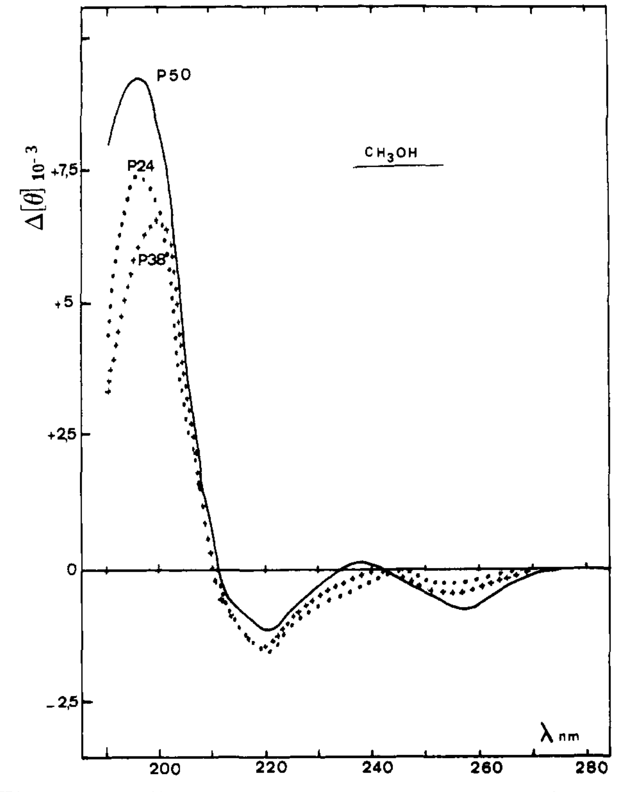


Figure 10. Difference CD spectra Δ[θ] = $f(\lambda)$ for the different copolymers in methanol (see text).

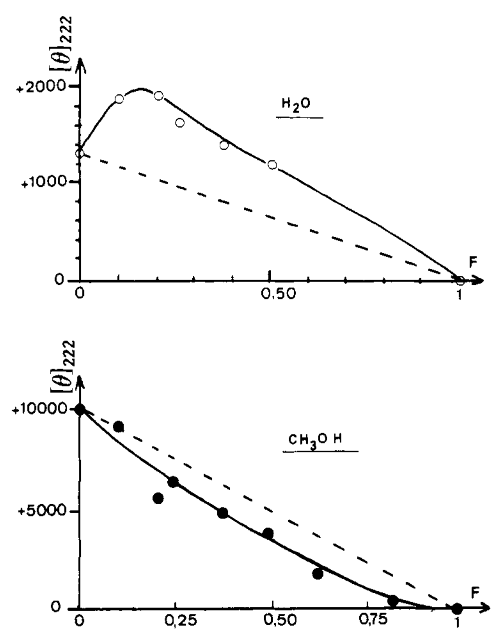


Figure 11. Composition dependence of $[\theta]_{222}$ in water (○) and methanol (●).

9 and 10 present such difference spectra in water and methanol. In water (Figure 9) the difference spectra consist of three bands: a weak negative band around 255 nm, a shoulder near 230 nm, and a strong positive band between 200 and 215 nm, depending on the composition of the copolymer. Two isodichroic points are found at 225 and 245 nm. In methanol, the two bands at 255 and 200 nm are more intense (especially the 200-nm band) and the position of the 200-nm band does not change with the composition of the polymer. The positive shoulder at 230 nm is replaced by a negative band at 220 nm. The negative band near 250 nm in water and methanol corresponds to the 240–242-nm band in the UV spectra and may be attributed to the allowed ^1L_A transition. The forbidden ^1L_B transition, which should be located at higher wavelength, is not observed because of the overlapping with the stronger 255-nm band, except for P14 in methanol, where a very weak positive band is observed around 265 nm ($[\theta] \sim +50$ deg·cm^2·dmol^{-1}) (Figure 8). The band near 200 nm must be related to the ^1B transition on the basis of its high intensity compared to the others. It is not split, in agreement with the absence of any ordered conformation, especially in methanol. The positive shoulder and the negative band in water and methanol (near 220–230 nm) are probably due to the $\pi \rightarrow \pi^*$ transition of the amide chromophore and the $n \rightarrow \pi^*$ transition of the carboxyl group in the chiral unit, perturbed by the presence of the aromatic residues of the achiral units. It is noteworthy that the induced Cotton effect of the achiral residue is more intense in methanol than in water, as is the case for the amide and carboxyl Cotton effect of the chiral unit (see Figures 3 and 4).

Figures 11–13 show the variation of $[\theta]$ with F at 222, 195, and 255 nm, respectively, in water and methanol. $[\theta]$ is calculated by taking into account the mean residue molecular weight M_r. Both kinds of residues are then considered as optically active species. Thus, $[\theta]$ is expeected not to be constant but to vary linearly with F, being zero when $F = 1$. At 222 nm, $[\theta]$ deviates appreciably from linearity, especially in water (Figure 11). This is explained by the positive Cotton effect at 230 nm in water and the negative Cotton effect at 220 nm in methanol, which have been attributed to perturbations of the chromophore of the *N*-methacryloyl-L-alanine residue. At 195 nm, $[\theta]$ changes nearly linearly with F in water, whereas a positive deviation from linearity is observed in methanol. In water, the induced positive ^1B Cotton effect lies between 200 and 215 nm and is about 4–8 times weaker than the negative Cotton effect of PNMA at 197 nm. Thus, the influence of the latter is predominant. In methanol, on the other hand, the induced positive Cotton effect (^1B) is very close to 195 nm (196–199 nm, Figure 10) and is much more intense than in water, giving a nonnegligible contribution (Figure 12).

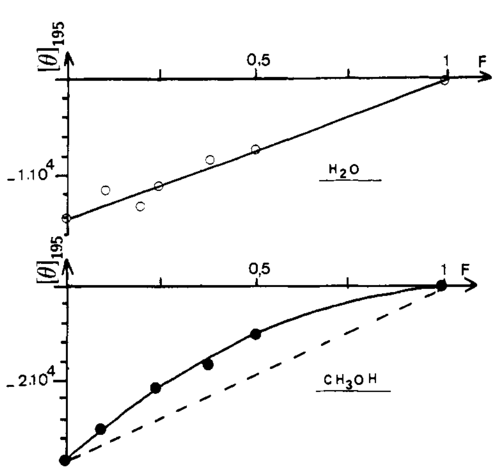


Figure 12. Composition dependence of $[\theta]_{195}$ in water (○) and methanol (●).

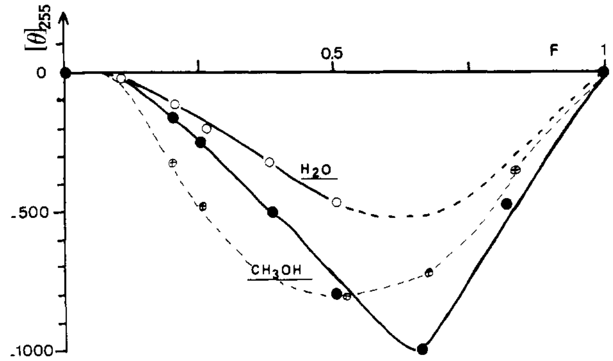


Figure 13. Composition dependence of $[\theta]_{255}$ in water (○) and methanol (●). Composition dependence of $[\theta]_{255}{}^a$ (per achiral unit) in methanol (⊕).

At 255 nm (Figure 13), three optically active transitions are to be considered: first, the weak $n \rightarrow \pi^*$ transition of the amide chromophore of the chiral residue and second, the ^1L_B and ^1L_A transitions of the aromatic chromophore, the last one being by far the more intense. In water, the absolute value of $[\theta]_{255}$ increases up to $F = 0.5$. Beyond this value, aqueous solutions of the copolymers are not optically clear. In methanol, $[\theta]_{255}$ increases up to $F = 0.63$ and then decreases. For a copolymer in which the achiral and chiral units are randomly distributed along the chain, it may be predicted that the optical activity induced in the achiral unit will be a maximum when the following two conditions are fulfilled: (i) the proportion of achiral units is high and (ii) each achiral unit still has two chiral units in its immediate vicinity. For an ideal random copolymer, both conditions are fulfilled when $F = 0.50$. Figure 13 shows that the molar ellipticity at 255 nm per achiral group, $[\theta]_{255}{}^a = [\theta]_{255}/F$, is actually a maximum for $F = 0.50$.

For block copolymers, on the other hand, induced optical activity is not observed and $[\theta]$ changes linearly with F, as for a mixture of two homopolymers (i.e., the two kinds of units are optically independent).[26] The results shown in Figure 13 are thus a further argument that our copolymers are random.[7]

Conclusion

The chiroptical properties of poly(*N*-methacryloyl-L-alanine) (PNMA) and of its model molecule, *N*-isobutyroyl-L-alanine (NIBA), in different solvents may be explained on the basis of contributions from the following transitions: (i) the $n \rightarrow \pi^*$ transition of the amide chromophore near 240–260 nm, (ii) the $\pi_1 \rightarrow \pi^*$ transition of the amide chromophore near 222 nm, (iii) the $n \rightarrow \pi^*$ transition of the carboxyl chromophore at 207 nm, (iv) the $\pi_2 \rightarrow \pi^*$ or $n \rightarrow \sigma^*$ transition of the amide chromophore near 190 nm, and (v) at least two other contributions below 190 nm: the $n \rightarrow \sigma^*$ or $\pi_2 \rightarrow \pi^*$ transition of the amide group and the $\pi \rightarrow \pi^*$ transition of the carboxyl groups.

CD spectra of PNMA are very close to those of NIBA, which shows that the contribution of the macromolecular conformation to the chiroptical properties is negligible. For the copolymers, three additional transitions are optically active in the accessible wavelength range, due to induction of optical activity by the neighboring chiral units: (i) the ^1L_B transition, weak, near 265–290 nm; (ii) the ^1L_B transition, near 250 nm; and (iii) the ^1B transition, very intense, around 200 nm. In addition, the electronic transitions of the chiral residue are perturbed by the proximity of the achiral unit. The nonlinear variations of the optical activity with the composition of the copolymers may be explained as arising from the above induced optically active transitions. It must be emphasized that the induced optical activity is observed even though no ordered conformation of the macromolecular chain exists.

In methanol, PNMA and all the copolymers are randomly coiled. In water, on the other hand, copolymers with $F > 0.15$ take a tightly coiled compact conformation. Despite this difference in their conformations, the dichroic spectra are very similar. The influence of the conformation and of the pH-induced or solvent-induced conformational transition of the copolymers on their chiroptical properties has been investigated in detail. The results of this work will be reported in a forthcoming paper.

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Registry No. *N*-Isobutyroyl-L-alanine, 81524-47-2; poly(*N*-methacryloyl-L-alanine), 77349-79-2; *N*-methacryloyl-L-alanine-/*N*-phenylmethacrylamide copolymer, 77349-80-5.

References and Notes

(1) J. Morcellet-Sauvage, M. Morcellet, and C. Loucheux, *Makromol. Chem.*, **182**, 949 (1981).
(2) J. Morcellet-Sauvage, M. Morcellet, and C. Loucheux, *Makromol. Chem.*, **183**, 821 (1982).
(3) J. Morcellet-Sauvage, M. Morcellet, and C. Loucheux, *Makromol. Chem.*, **183**, 831 (1982).
(4) J. Morcellet-Sauvage, M. Morcellet, and C. Loucheux, submitted to *Polym. Bull.*
(5) M. Morcellet, C. Loucheux, and H. Daoust, *Macromolecules*, **15**, 890 (1982).
(6) P. Pino, F. Ciardelli, and M. Zandomeneghi, *Annu. Rev. Phys. Chem.*, **21**, 561 (1970).
(7) J. Morcellet-Sauvage, Thesis, Lille, France, 1982.
(8) M. Vert, in "Charged and Reactive Polymers", E. Selegny, Ed., D. Reidel Publishing Co., Dordrecht, Holland, 1974, Vol. 1, pp 347–370.
(9) M. Vert, in "Charged and Reactive Polymers", E. Selegny, Ed., D. Reidel Publishing Co., Dordrecht, Holland, 1979, Vol. 5, pp 291–316.
(10) C. Braud and M. Vert, *Isr. J. Chem.*, **15**, 39 (1976/1977).
(11) C. Braud, M. Vert, and E. Selegny, *Makromol. Chem.*, **175**, 775 (1974).
(12) C. Braud and M. Vert, *Polymer*, **16**, 115 (1975).
(13) C. Braud and M. Vert, *Polym. J.*, **12**, 785 (1980).
(14) C. Villiers, C. Braud, M. Vert, E. Chiellini, and M. Marchetti, *Eur. Polym. J.*, **14**, 211 (1978).
(15) C. Villiers, C. Braud, M. Vert, and E. Chielleni, *Macromolecules*, **12**, 103 (1979).
(16) R. K. Kulkarni and H. Morawetz, *J. Polym. Sci.*, **54**, 183 (1961).
(17) K. Ulbrich and J. Kopecek, *Eur. Polym. J.*, **12**, 183 (1976).
(18) A. Burovoy, *J. Chem. Soc.*, 1177 (1939).
(19) V. Madison and J. Schellman, *Biopolymers*, **9**, 511 (1970).
(20) H. H. Jaffe and M. Orchin, in "Theory and Applications of U.V. Spectroscopy", Wiley, New York, 1962, p 180.
(21) I. Listowsky, G. Avigad, and S. Englard, *J. Org. Chem.*, **35**, 1080 (1970).
(22) E. B. Nielsen and J. A. Schellman, *J. Phys. Chem.*, **71**, 2297 (1967).
(23) D. W. Urry, *J. Phys. Chem.*, **72**, 3035 (1968).
(24) C. Carlini, F. Ciardelli, and P. Pino, *Makromol. Chem.*, **119**, 244 (1968).
(25) H. Yamaguchi and Y. Minoura, *J. Polym. Sci., Part A-1*, **8**, 1467 (1970).
(26) H. Yuki, K. Ohta, and N. Yajima, *Polym. J.*, **1**, 164 (1970).
(27) B. Katz, M. Brith, B. Sharf, and J. Jortner, *J. Chem. Phys.*, **54**, 3924 (1971).
(28) H. E. Ungnade, *J. Am. Chem. Soc.*, **75**, 432 (1953).
(29) A. O. Barel and A. N. Glazer, *Biopolymers*, **7**, 275 (1969).
(30) L. Verbit, *J. Am. Chem. Soc.*, **87**, 1617 (1965).
(31) J. Beaumais, Thesis, Rouen, France, 1978.
(32) W. Gaffield and W. G. Galetto, *Tetrahedron Lett.*, **27**, 915 (1971).
(33) P. Salvadori, in "Charged and Reactive Polymers", E. Selegny, Ed., D. Reidel Publishing Co., Dordrecht, Holland, 1979, Vol. 5, pp 225–230.
(34) P. Salvadori, L. Lardicci, R. Menicagli, and C. Bertucci, *J. Am. Chem. Soc.*, **94**, 8598 (1972).