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Optically Active Polyelectrolytes with Variable Hydrophobicity. 3. Effects of pH-Induced Chromophore and Conformation Changes on Chiroptical Properties of Alternating Copolymers of Maleic Acid and Optically Active 1-Methylalkyl Vinyl Ethers

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ABSTRACT: Large modifications in ORD and CD spectra of three optically active maleic acid/alkyl vinyl ether alternating copolymers (MAc/R*VE with R* = (*S*)-1-methylpropyl, sample C4$_1$; R* = (*R*)-1-methylbutyl, sample C5$_1$; and R* = (*S*)-1-methylheptyl, sample C8$_1$) were found after adding an alkaline reagent to aqueous or methanolic solutions. When progressively ionized in water, these three polyelectrolytes show different conformational behaviors (respectively chain extension, compact coils-to-extended coils transition, and polysoap-like structure) depending on the length and, thus, on the hydrophobic character of etheral side-chain alkyl substituents. These differences of conformational behavior are not reflected in the observed pH-induced optical activity changes which primarily depend on chemical modifications of asymmetrically perturbed carboxyl chromophores and on consequent perturbations of the other chromophoric systems. The possibility for a folding of side chains on the polymeric backbone explaining the alkyl chain-length dependence of observed CD bands in water but not in methanol whatever the degree of neutralization is discussed.

In the field of optically active polymers, optical rotatory dispersion (ORD) and circular dichroism (CD) have been used mostly for structural studies.[1,2] They have provided us with a lot of relevant information on macromolecular conformations for helical biopolymers (poly(α-amino acids), polynucleotides, etc.)[3] and for some synthetic

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analogues.[4] In contrast, only limited structural information has been obtained for randomly coiled optically active polymers because of the following: first, the ignorance of the properties of unusual chromophores, and second, the rather large number of allowable chain conformations in the absence of high stereoregularity and of intramolecular interactions needed to stabilize ordered secondary structures.[5]

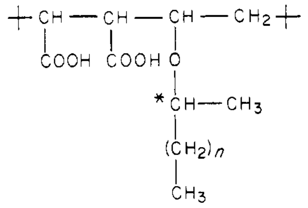
However, it has been shown that information on the chemical behavior of randomly coiled optically active polymers can be drawn from their optical activity. Accordingly, the investigation of relative effects of chemical and conformational modifications on the optical activity of reactive optically active polymers other than biopolymers has received increasing interest in the last years.[5-8]

As a part of this investigation, weak polyacids have been considered because of their reversible and easy-to-do chemical and conformational changes which are controlled by the pH-induced ionization process.[9-11] However, some polyacids can show particular conformational behavior in water solution when interacting hydrophobic groups are present within the polymer backbone or side chains (compact coils-to-extended coils transition[12,13] or polysoap-like structure[14]).

In order to determine if ORD and CD can reflect such special conformational behaviors, we have undertaken the study of optically active polyelectrolytes having similar chemical properties but completely different pH-dependent conformational behaviors according to the presence of different hydrophobic substituents along the chains.

In a previous paper,[15] we have reported the case of acrylic acid/(+)-*N*-(*sec*-butyl)-*N*-methylacrylamide random copolymers for which hydrophobicity varied according to the content of hydrophobic amide repeating units. Macromolecules with less than 20% of the amide repeating units behaved as poly(acrylic acid) while those with a higher percentage collapsed at low values of the degree of ionization. CD spectra of two copolymers having respectively ~10 and ~38% of amide repeating units were compared. For the latter, no CD particularity assignable to the compactly coiled structure was detected.

As another example, a series of three alternating maleic acid/chiral alkyl vinyl ether copolymers (MAc/R*VE's) have been synthesized:[16]



$$\left[\mathrm{CH(COOH)-CH(COOH)-CH(O{-}{}^{*}CH(CH_3)(CH_2)_nCH_3)-CH_2}\right]$$

n	R*	copolymer
1	(*S*)-1-methylpropyl	$C4_1$
2	(*R*)-1-methylbutyl	$C5_1$
5	(*S*)-1-methylheptyl	$C8_1$

This kind of alternating copolymer offered us the possibility of changing the hydrophobic character of a well-defined polyelectrolytic chain through the alkyl substituent of vinyl ether moieties without significant modification of the polymer backbone and of side-chain structures (the asymmetric carbon atom in the starting ethereal comonomer being in all cases in the α position with regard to the oxygen atom) and without any loss of chiral groups (contrary to the case of acrylic copolymers previously studied for which the hydrophobicity was lowered by taking off some of the chiral amide moieties).[15]

From potentiometric, viscometric, and dye-solubilization investigations, it has been shown that the $C4_1$ copolymer behaves as a "normal" polyelectrolyte (its chains progressively extend when the charge density increases). In contrast, the highly hydrophobic $C8_1$ copolymer behaves like a polysoap while $C5_1$ copolymer of intermediate hydrophobicity presents a pH-induced compact coils-to-extended coils conformational transition over a range of low values of the degree of ionization.[17]

In this paper, we report the variations of the optical activity (ORD and CD) of these three copolymers when carboxylic groups ionize. These variations are discussed with regard to the different conformational behaviors of $C4_1$, $C5_1$, and $C8_1$ copolymers and with regard to the modification of chromophores because of COOH group ionization.

Experimental Section

Materials. The synthesis and the characterization of $C4_1$, $C5_1$, and $C8_1$ copolymers were previously reported.[16,18] Characteristics of the three copolymers have been reported in Table II of ref 16.

For the sake of homogeneity in the comparison with samples $C4_1$ and $C8_1$ of *S* configuration, the signs of optical activity data of the $C5_1$ copolymer of *R* configuration have been changed and are thus referred to a copolymer as obtained from the (*S*)-1-methylbutyl vinyl ether enantiomer.

Conditioning of Water Solutions. Salt-free aqueous solutions of the three copolymers were obtained by precolating alkaline solution through a cation exchange column (H^+ form). Then, potassium hydroxide was used to adjust the ionization state as previously described.[17]

Conditioning of Methanol Solutions. Solutions of freeze-dried copolymer samples were obtained by direct dissolution in spectrograde methanol. A methanol solution of sodium methoxide, titrated with benzoic acid in dimethylformamide, was used to adjust the degree of neutralization of COOH groups at desired values.

ORD and CD Measurements. ORD and rotatory power variations at a fixed wavelength were determined at different ionization states by using a "Spectropol I" FICA spectropolarimeter thermostated at 25.0 °C. CD curves and ellipticity variations at a fixed wavelength were recorded by using a JASCO J 40 B dichrometer at room temperature, the optical pathway being flushed with nitrogen.

Results and Discussion

The optical activity changes studied in this work were obtained by addition of an alkaline reagent to polyacid solutions [C_p = molar concentration in dibasic repeat units] and thus by raising the pH of the solution. However, the pH is not a suitable variable to correlate the optical activity to the ionization reaction.[15] The correlation is better shown when the ratio $\tau = [\mathrm{OH^-}]_{\mathrm{added}}/C_p$ (analogous to the degree of neutralization) is used as a variable, especially for polydibasic acids like MAc/R*VE's. Under the selected experimental conditions, the neutralization of the first acidity of MAc/R*VE's occurred for $0 < \tau < 1.0$ while the second acidity neutralized for $1.0 < \tau < 2.0$. Furthermore, τ allowed us to characterize the excess of alkaline reagent (if present) with regard to the polymer concentration and not to the pH. The ionic strength (μ) is known to greatly influence the conformational behavior of polyelectrolytes. During the neutralization of the first and the second acidity, the ionic strength was $\mu = 0$. For $\tau > 2.0$, an ionic strength was generated by the excess of alkaline reagent. The value of μ was connected to the polymer concentration C_p according to $\mu = (\tau - 2)C_p$.

pH-Induced ORD Changes in Water. ORD curves of $C4_1$, $C5_1$, and $C8_1$ copolymers in water at different state of ionization are plotted in Figure 1. Abnormal positive curves (according to the nomenclature of Lowry[19]) ob-

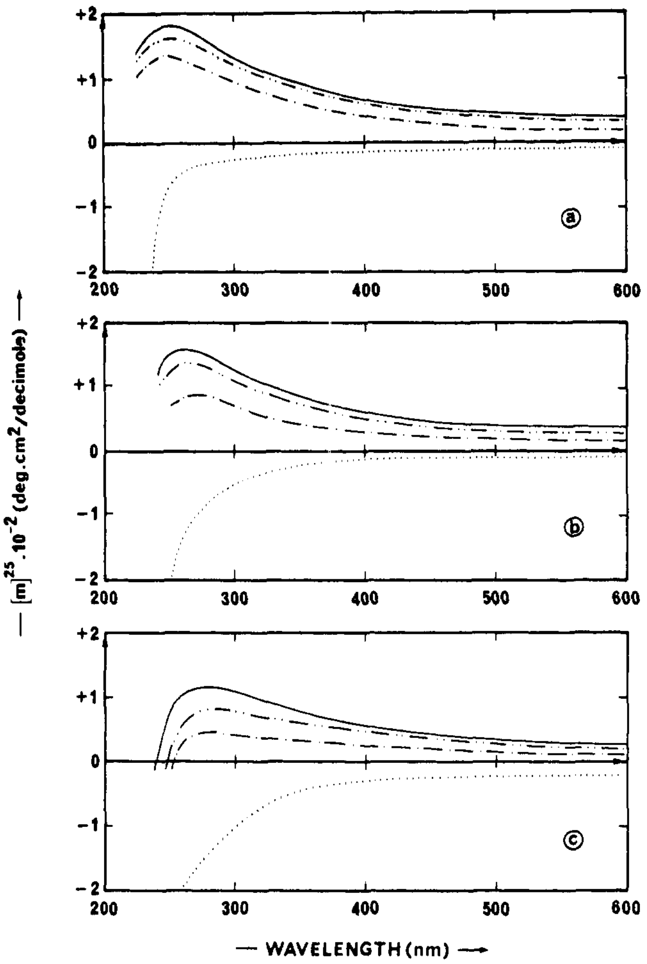


Figure 1. ORD curves of alternating copolymers of maleic acid and alkyl vinyl ether MAc/R*VE in water at different values of τ (τ = 0, —; τ = 0.3, ··–; τ = ·–·; τ = 1.0, ·—·; τ = 2.0, ···): (a) C4$_1$; (b) C5$_1$; (c) C8$_1$.

served at $\tau = 0$ were already reported and discussed.[16]

Important modifications of ORD curves occurred when the degree of neutralization was increased. For $0 < \tau < 1.0$, optical rotations decreased but ORD curves kept similar positive and abnormal shapes. In contrast, drastic changes were found when going from $\tau = 1.0$ to 2.0. Both optical rotations and ORD curves changed sign and the latter turned out to be normal above 250 nm. At last, when both carboxylic groups were neutralized ($\tau > 2$), the three copolymers showed similar ORD curves as far as shape and magnitude are concerned.

pH-Induced CD Changes in Water. Figure 2 shows CD spectra corresponding to the ORD curves above. For the three copolymers, the CD spectrum at $\tau = 0$ consists of a broad negative band centered at $\simeq$215 nm.[16] This band has been assigned to the n $\rightarrow \pi^*$ electronic transitions of COOH chromophores disymmetrically perturbed by chiral centers present in the adjacent ethereal structural moieties. Its magnitude increased in negative values when going from C4$_1$ to C8$_1$.[16]

When going from $\tau = 0$ to 1.0, the negative CD bands centered at $\simeq$215 nm are modified (Figure 2). For C4$_1$ copolymer, the negative maximum shifts toward low wavelengths ($\simeq$205 nm). It decreased in magnitude while a very small positive band appeared with a maximum at about 235 nm. C5$_1$ copolymer showed similar trends but with larger magnitudes. As to C8$_1$ copolymer, its negative band was also blue shifted but no positive ellipticity appeared around 235 nm. Maybe the weak positive CD contribution found for C4$_1$ and C5$_1$ above 220 nm also exists for C8$_1$ but it overlaps with the negative band much stronger in C8$_1$ than in the two other compounds.

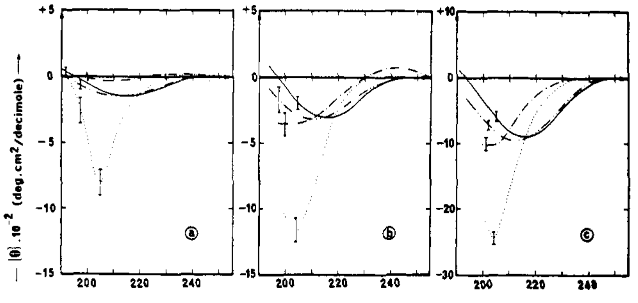


Figure 2. CD curves of MAc/R*VE copolymers in water at different values of τ (τ = 0, —; τ = 0.3, ··–; τ = 1.0, ·–·; τ = 2.0, ···): (a) C4$_1$; (b) C5$_1$; (c) C8$_1$.

During the increase of τ from 1.0 to 2.0, the negative CD band located at about 205 nm increased in magnitude in all cases without any apparent change in position.

At last, when the two acidic groups were ionized, CD spectra of the three copolymers appeared similar in shape but still different in magnitude since the 205 nm negative CD band was three times larger for C8$_1$ than for C4$_1$ copolymer. Under the same conditions, ORD curves have been found almost identical in shape and in magnitude. This difference between ORD and CD is probably due to the fact that optical rotations in the visible depend primarily on strong far-UV Cotton effects while observed CD bands depend on weak local Cotton effects as previously discussed for $\tau = 0$.[16]

The use of Kronig–Kramers transforms to show the contributions of far-UV electronic transitions and their modifications when τ was varied was not possible because of too many unknowns concerning the number and location of the Cotton effects. Furthermore, it is possible that the negative CD bands observed at $\simeq$215 nm for $\tau = 0$ result from the overlapping of two n $\rightarrow \pi^*$ transitions due to the presence of two different carboxyl chromophores in repeating alternating units. The presence of two optically active electronic transitions in this region of the spectrum would well account for the bisignate shape of the CD curves at $\tau = 1.0$ (Figure 2) if one admits that one of these two Cotton effects changes sign as τ increases. The positive part of the bisignate CD curves observed at $\tau = 1.0$ for C4$_1$ and C5$_1$ copolymers could also come from the foot of a large positive CD band located farther in the UV. A detailed study of optically active monoacid model compounds would be necessary to clear up this point.

In spite of the complexity of the phenomena in the accessible region of the spectrum ($\lambda > 185$ nm), modifications of inaccessible Cotton effects, when COOH ionized, can be obviously shown on the basis of inconsistencies in the comparison of relative variations of ORD and CD spectra. As an example, when τ increased from 0 to 1.0, a shift of ORD curves toward higher positive rotations is expected for the three copolymers because of the blue-shifted negative CD band as well as the appearance of a weak positive band for C4$_1$ and C5$_1$ copolymers. One actually observes a shift to lower positive rotations in agreement with the presence of a negative contribution arising from the modification of far-UV Cotton effects.

Except for the difference of magnitude of their CD spectra, the three polyelectrolytes showed rather similar optical activity changes when succinic moieties were ionized and these changes seemed to be independent of their conformational behaviors. In order to confirm this point, variations of both optical rotation and ellipticity have been investigated in more detail at fixed wavelengths.

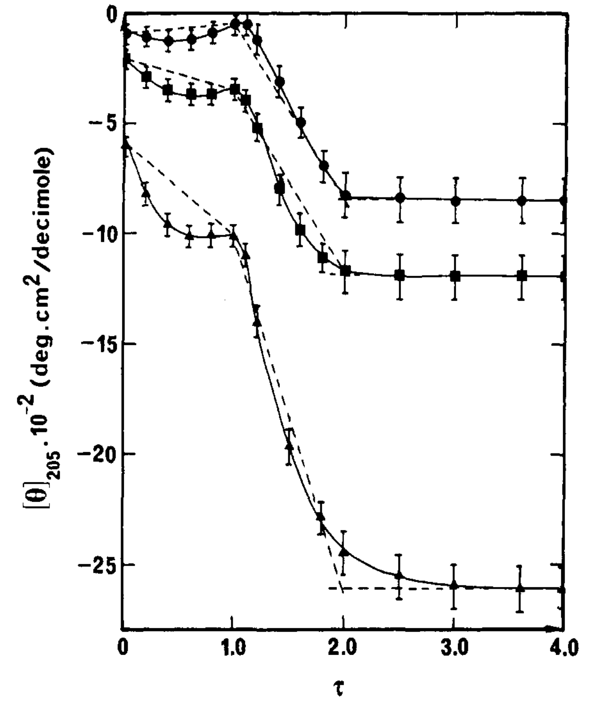


Figure 3. Variation of molar ellipticity $[\theta]_{205}$ as a function of τ for $C4_1$ (●), $C5_1$ (■), and $C8_1$ (▲) copolymers in water ($C_p = 1 \times 10^{-2}$ mol/L). Dotted lines figure linear variations of $[\theta]_{205}$ as usually found when ionizing low molecular weight model compounds.

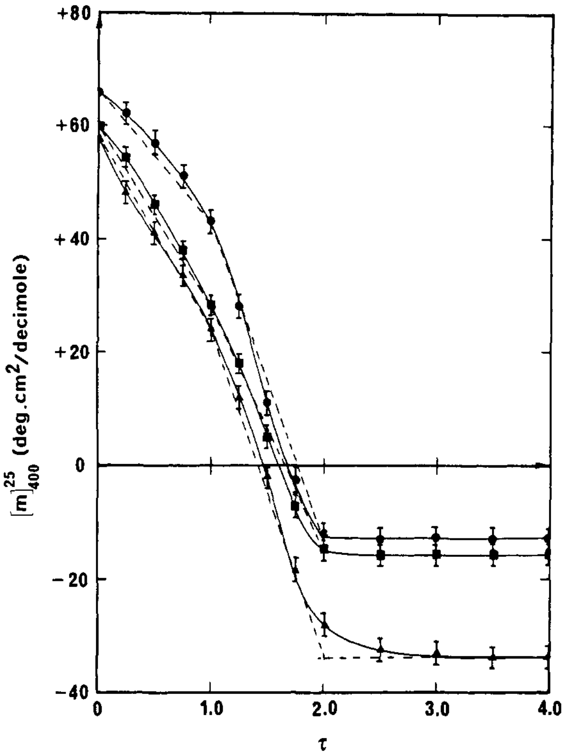


Figure 4. Variation of molar optical rotation $[m]^{25}_{400}$ as a function of τ for $C4_1$ (●), $C5_1$ (■), and $C8_1$ (▲) copolymers in water ($C_p = 1 \times 10^{-2}$ mol/L). Dotted lines figure linear variations of $[m]^{25}_{400}$ as usually found when ionizing low molecular weight model compounds.

pH-Induced Optical Activity Changes at a Fixed Wavelength in Water. Changes of molar ellipticity $[\theta]$ at 205 nm when acidic groups ionized are shown in Figure 3 for the three copolymers. A break was found at the end of the neutralization of the first acidic groups ($\tau = 1.0$). Then $[\theta]_{205}$ decreased rapidly when τ increased. A second break occurred at $\tau = 2.0$ for $C4_1$ and $C5_1$ copolymers. For $\tau > 2.0$, the molar ellipticity remained constant although macromolecular conformations continue to change because of the ionic strength generated by the excess of alkaline reagent. In Figure 3, the ionic strength reached $\mu = 0.02$ at $\tau = 4.0$.

For the $C8_1$ copolymer a smooth variation around $\tau = 2.0$ instead of a break led to constant molar ellipticity for $\tau > 3$ only. The absence of a sharp break is attributed to the effect of the hydrolysis of the carboxylate salt corresponding to the second acidity which is weaker for $C8_1$ than for $C4_1$ and $C5_1$. Therefore, τ is no longer equal to the degree of neutralization around $\tau = 2.0$. An excess of alkaline reagent was needed to ionize all the COOH groups and to obtain the constancy of $[\theta]_{205}$. This interpretation is confirmed by the fact that the tangent to linear parts of the $C8_1$ curve in Figure 3 intercepts at $\tau = 2.0$.

Figure 4 shows the variation of $[m]^{25}$ at 400 nm as a function of τ for $C4_1$, $C5_1$, and $C8_1$ copolymers. $[m]^{25}_{400}$ decreased for $0 < \tau < 2.0$ with a little change of slope for $\tau = 1.0$. Beyond $\tau = 2.0$, the molar rotatory power remained constant for all copolymers but $C8_1$. For the latter, the smooth variation around $\tau = 2.0$ has also been attributed to the hydrolysis of the salt as discussed above.

Although more electronic transitions are involved in optical rotation variations than in the ellipticity ones, it is obvious that the shape of curves reported in Figures 3 and 4 is quite similar whatever the copolymer and its conformational behavior in water solution. Nothing particular was detected for $C5_1$ copolymer (which shows a compact coils-to-extended coils transition) as compared to $C4_1$ (whose chains progressively extend) and to $C8_1$ which keeps compactly coiled conformations when acidic groups ionize. The nonlinearity of variations observed during the neutralization of each of the two acidic groups is not connected to any conformational behavior but depends only on the content of ionized and unionized repeat units which are spectroscopically dependent of each other since they belong to the same macromolecule.[5,15]

Accordingly, for MAc/R*VE copolymers, one can conclude that variations of optical rotations, when τ is varied, depend primarily on the chromophores perturbed by the ionization of COOH groups and not on the conformational behavior of main chains.

The only thing which appeared to be connected to the length of the ethereal alkyl side chains was the magnitude of COOH n → π* CD bands. Indeed, the magnitude of the 215-nm CD band in each of the three copolymers at $\tau = 0$ was already found to be very different in water but almost identical in ethanol.[16] Furthermore, Figure 2 obviously shows that the ellipticities of all three copolymers remain different whatever the degree of neutralization.

In order to confirm this feature, CD changes have been investigated while $C4_1$, $C5_1$, and $C8_1$ copolymers were neutralized in methanol, a solvent known to supress hydrophobic interactions in polyacids when added to water.[13,20]

CD Changes When Ionizing COOH in Methanol. CD spectra of $C4_1$, $C5_1$, and $C8_1$ copolymers in methanol were carried out at different values of the degree of neutralization which were adjusted by using a methanolic solution of sodium methoxide (Figure 5).

Under these conditions, the negative CD band at 205 nm was found to have the same magnitude for the three copolymers at $\tau = 0$ and $\tau = 2.0$. At $\tau = 1.0$, slight differences in magnitude appeared but the CD spectra still looked similar, showing the presence of both a negative and a positive band, the latter being very small for all but for $C5_1$.

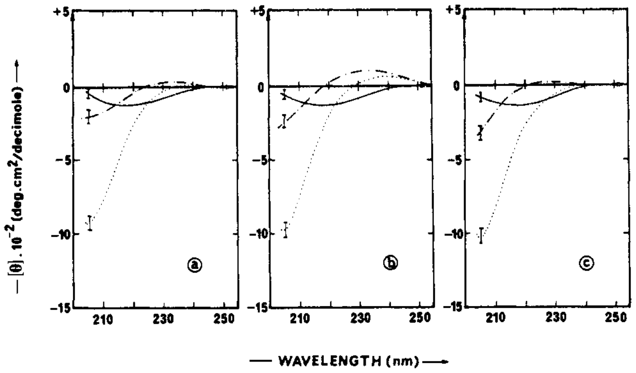


Figure 5. CD curves of MAc/R*VE copolymers in methanol at different values of τ (τ = 0, —; τ = 1.0, •–•; τ = 2.0, •••: (a) $C4_1$; (b) $C5_1$; (c) $C8_1$.

Therefore, changes in the CD spectra when τ increased in methanol appeared similar to those observed in water (Figure 2) as far as the shape of curves is concerned.

It is of interest to point out that the CD spectrum of the $C8_1$ copolymer in methanol at $\tau = 1.0$ revealed a very small positive ellipticity above 220 nm. This positive ellipticity supports the statement made previously for water solutions that $C8_1$ copolymer probably behaves as $C4_1$ and $C5_1$ as far as the number and the position of CD bands are concerned.

Since the "disorder-to-disorder" conformational transition of $C5_1$ copolymer is not reflected by ORD and CD and since ORD is much less sensitive to the side-chain length than CD, we conclude that the differences in magnitude of $n \rightarrow \pi^*$ electronic transition of carboxylic groups (whatever the value of τ) are closely related to local conformations of the ethereal side chain.

It is likely that in a poor solvent for alkyl moieties such as water, the long aliphatic side chains of $C8_1$ copolymer have a larger affinity for the polymer backbone than for the solvent. This statement is supported by the observed polysoap structure in water. In contrast, less hydrophobic short alkyl chains of $C4_1$ are probably partially solvated by water through the ethereal function as suggested by the opened coil conformations of this polyelectrolyte. Accordingly, asymmetric centers located in the side chain would be in a more rigid environment in $C8_1$ copolymer than in $C4_1$ and $C5_1$. This fact as well as a change in the average position with regard to carboxylic acid chromophores could explain the magnification of the $C8_1$ CD band as compared to the $C5_1$ and $C4_1$ ones.

In methanol, where effects of hydrophobic interactions usually vanish, better solvation of ethereal side chains should prevent their folding on the backbone, leaving asymmetric centers statistically located at the same position, whatever the chain length. In agreement with this interpretation, CD spectra of $C4_1$, $C5_1$, and $C8_1$ copolymers which are similar to each other are also similar to that of the well solvated $C4_1$ copolymer in water as shown by comparing Figures 2 and 5.

Once again, the ionization of COOH groups is the main factor which affects the optical activity of polyacids when the pH is increased in water. The differences in conformational behavior of $C4_1$, $C5_1$, and $C8_1$ copolymers were not reflected in optical activity changes. However, the choice of these three very similar copolymers allowed us to show that local side-chain conformations, which depend on solvophobic interactions, affect the magnitude of weak $n \rightarrow \pi^*$ Cotton effects of carboxylic chromophores in water in the absence of any ordered secondary structure. The perturbation is not proportionally extended to all optically active electronic transitions. This fact explains that optical rotations in the visible range (which depend on far-UV Cotton effects) only slightly reflect the effect of side-chain folding on the polymer backbone.

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