O.r.d.–c.d. and protonation of amide-containing polymers in strong acid media: 1. The case of poly(–)1,2-diaminopropane sebacamide, an optically active nylon-type polyamide

Michel Vert, Christian Braud and Yovanka Huguet
Laboratoire de Chimie Macromoléculaire, ERA CNRS 471, *Faculté des Sciences et des Techniques, Université de Haute-Normandie,* 76130 *Mont-Saint-Aignan, France*
(*Received* 20 *February,* 1981)

Optical rotatory dispersion (o.r.d.) and circular dichroism (c.d.) of poly(–)1,2-diaminopropane sebacamide I and of its model compound, *N-N'*-didecanoyl (–)1,2-diaminopropane II, are investigated in trifluoroethanol-formic acid, -trifluoroacetic, -methanesulphonic and -sulphuric acid mixtures, with emphasis on the two latter solvent systems. It is shown that the optical activity of both compounds depends on the nature and the concentration of the acid. The stronger the acid, the larger the chiroptical changes observed for a given value of the acid/amide molar ratio *r*. The drastic changes caused by small amounts of methanesulphonic and sulphuric acids are assigned to protonation of amide chromophores solely.

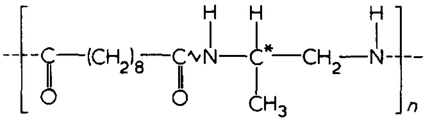
INTRODUCTION

In strong acid media, nylon-type polyamides[1–2] and poly-α-amino-acids[3–4] exhibit anomalous concentration dependences of reduced viscosity parameters that have been considered as resulting from polyelectrolytic effects owing to the protonation of amide groups. On the other hand, increasing concentration of strong organic or inorganic acids are known to cause drastic o.r.d. and c.d. changes in the case of polypeptides[5–13] and of optically active nylon-type polyamides with more or less rigid chains[14–21].

The existence of relationships between o.r.d. and c.d. changes, acid-base properties and order-to-disorder conformational transitions of amide-containing polymer chains has been questioned many times, but the answers are still unclear. The examination of o.r.d. and c.d. of polymers in media where parts of the chains can undergo chemical reactions is hampered because generally it is difficult to determine whether changes in the spectral patterns are related to conformational variations, specific solvent effects, chemical modifications of chromophores, or to a combination of these phenomena[22–23].

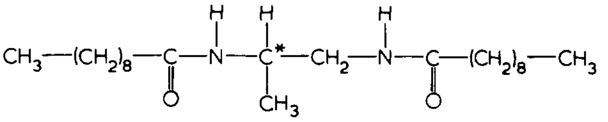
We suggested[22] and later showed for various specific cases[24–28], that the problem can be simplified if polymers with flexible non-stereoregular chains are considered. These chains cannot take on ordered conformations in solution and thus, changes in optical activity primarily reflect chemical modifications of chromophores, with no contribution from macromolecular conformations[23]. Therefore, the study of o.r.d. and c.d. changes of non-stereoregular amide-containing polymers in strong acid media presents a special interest. It should indicate what might be the effects of protonation of amide chromophores on the chiroptical properties of stereo-ordered polyamides, and especially polypeptides, in the absence of order-to-disorder conformational transition. Accordingly, we have examined the optical activity of a series of non stereo-ordered amide-containing polymers in various strong acid media.

In this paper, we wish to report acid-induced chiroptical property changes of a nylon-type polyamide, poly(-)1,2-diaminopropane sebacamide I, and of its model compound, *N-N'*-didecanoyl (-)1,2-diaminopropane II, in alcoholic solutions.



$$\left[-\underset{\underset{O}{\|}}{C}-(CH_2)_8-\underset{\underset{O}{\|}}{C}\sim\overset{H}{\overset{|}{N}}-\overset{H}{\overset{|}{\underset{\underset{CH_3}{|}}{C^*}}}-CH_2-\overset{H}{\overset{|}{N}}- \right]_n$$

(I)



$$CH_3-(CH_2)_8-\underset{\underset{O}{\|}}{C}-\overset{H}{\overset{|}{N}}-\overset{H}{\overset{|}{\underset{\underset{CH_3}{|}}{C^*}}}-CH_2-\overset{H}{\overset{|}{N}}-\underset{\underset{O}{\|}}{C}-(CH_2)_8-CH_3$$

(II)

Though the asymmetric carbon atoms of the main chain have the same configuration, polymer I is not stereoregular because of the dissymmetry of the diamine moiety which allows head-to-head and head-to-tail arrangements as represented by the ∼ link in the formula.

EXPERIMENTAL

Poly(-)1,2-diaminopropane sebacamide was prepared by fast stirring of (-)1,2-diaminopropane (0.4 M in water) and sebacoyl chloride (0.4 M in CCl_4) solutions using sodium bicarbonate as proton acceptor according to a usual procedure for interfacial polycondensation[29].

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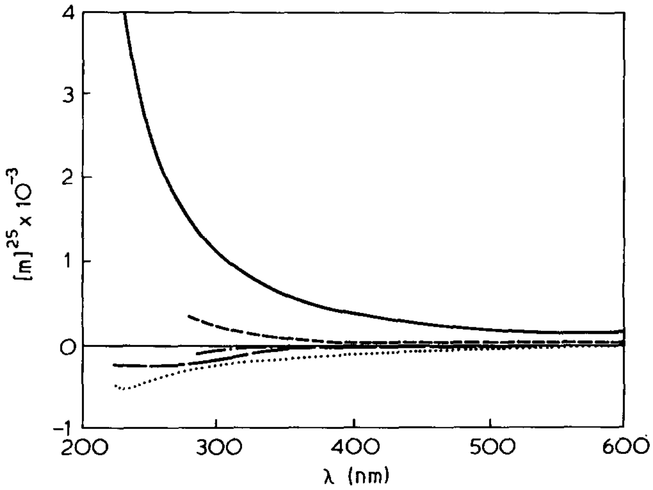

Figure 1 O.r.d. spectra of polyamide I in TFE ——; FA – – – –; TFA —·—·—; MSA —— —— and H_2SO_4 ·····

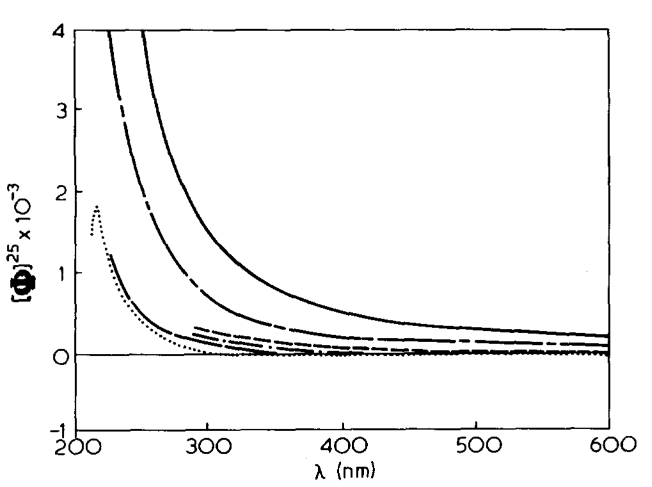

Figure 2 O.r.d. spectra of model compound II in TFE ——; methanol — — — —; FA – – – –; TFA —·—·—; MSA —— —— and H_2SO_4 ·····

N-N′-didecanoyl (-)1,2-diaminopropane (Mp = 138°C) was synthesized by reacting decanoyl chloride with (-)1,2-diaminopropane as reported elsewhere[30].

Alcohols and acids were of analytical grade and were used without further purification.

O.r.d. spectra were carried out by using a Spectropol I FICA spectropolarimeter thermostated at 25°C.

C.d. spectra were obtained at room temperature on a JASCO J 40 B dichrometer purged with dry nitrogen.

Alcohol/acid solutions of compounds I and II ($C = 6\times 10^{-3}$ M, as referred to residue $MW = 240$ for polymer I) were prepared either by weighting the desired amounts of acid in a 10 cm³ volumetric flask and adding suitable amounts of a 1.2×10^{-2} M stock solution of the compound, and of pure alcohol, or by mixing 6×10^{-3} M sample solutions of known contents in acid in order to have intermediate acid concentrations. The various solutions were always prepared from cooled components and all measurements were carried out within half an hour after preparation in order to forestall degradation.

RESULTS AND DISCUSSION

Figure 1 shows the o.r.d. spectra of polyamide I in trifluoroethanol (TFE) and in various acids (formic (FA); trifluoroacetic (TFA); methanesulphonic (MSA) and sulphuric. In pure TFE, the positive plain curve obeys the one-term Drude equation $[\alpha] = A/(\lambda^2 - \lambda_c^2)$ ($A = +19\times 10^{-8}$ deg cm^4 dg^{-1}; $\lambda_c = 216$ nm) i.e. is simple according to Lowry's definitions[31]. In contrast, o.r.d. curves in the acids are complex and have different signs depending on the acid (positive for FA, negative for TFA, MSA and H_2SO_4).

Figure 2 shows the o.r.d. spectra of model compound II in methanol, where polymer I is not soluble, in TFE and in the different acids already used for polymer I. O.r.d. curves are positive and simple in methanol ($A = +5.7\times 10^{-8}$; $\lambda_c = 218$ nm) and in TFE ($A = +14\times 10^{-8}$; $\lambda_c = 226$ nm). In contrast, the positive curves observed in the acids are all complex. The changes in optical rotation observed for polymer I and model compound II when going from pure TFE to pure acids depend on the acid concentration as evidenced in *Figure 3*. For a given concentration of polyamide I or model compound II, increasing the acid content, referred to as the acid/amide molar ratio τ, results in a decrease of the molar rotation (φ) which is initially positive in TFE. For FA, only a slow decrease is observed up to pure acid. For TFA, molar optical rotation decreases faster than for FA. The trend is still enhanced for MSA and H_2SO_4 where $[\varphi]$ drops steeply to negative values for low τ values. However, in the two latter acids, $[\varphi]$ rises up again smoothly as τ increases to its limit value which corresponds to pure acids. Similar curves were found for polymer I as exemplified in *Figure 3* for the TFE/MSA system. Therefore, the optical activity of both compounds depends on the nature and on the concentration of the acid. The stronger the acid, the larger the optical rotation changes for a given value of the acid/amide molar ratio.

These findings are confirmed by c.d. investigations. Because of light absorption, carboxylic acids were not suitable for c.d. measurements in the 200 nm wavelength range. H_2SO_4 and MSA caused similar changes but for magnitude. Only the case of the latter has been represented in *Figure 4*. In TFE, compounds I and II show similar c.d. patterns composed of a large positive band located at 197 nm and a weak negative contribution in the 220–230 nm region of the spectrum. The presence of a positive c.d. band has already been observed at 200 nm for compound II in methanol[32]. The band in TFE as well as the band in methanol probably result from overlapped

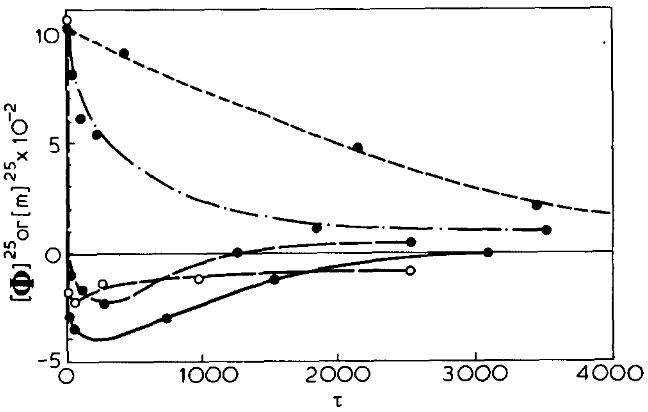

Figure 3 Changes of molar optical rotation at 320 nm in TFE/acid mixtures in regard to amide/acid molar ratio τ. FA – – – –; TFA —·—·; MSA —— —— and H_2SO_4 ——. Model compound II ●; polyamide I ○

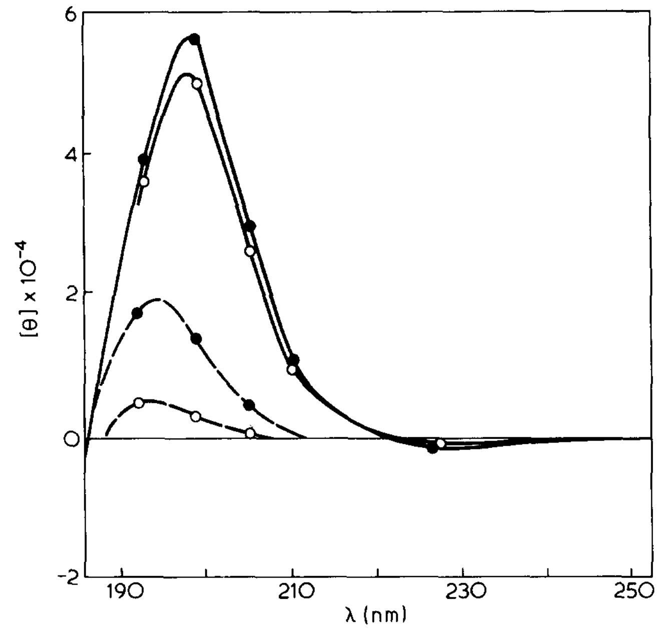

Figure 4 **C.d. spectra of polymer I ○ and model compound II ● in TFE ——— and MSA – – – –**

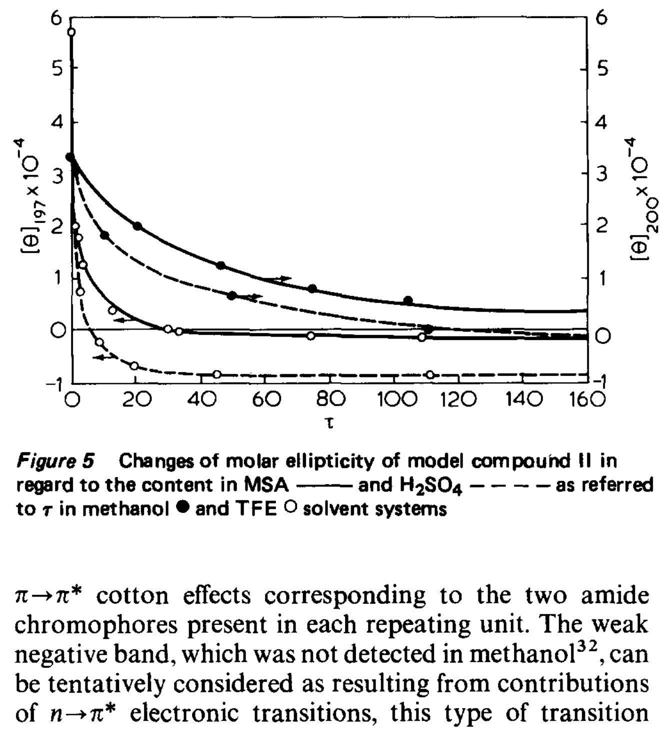

Figure 5 **Changes of molar ellipticity of model compound II in regard to the content in MSA ——— and H_2SO_4 – – – – as referred to τ in methanol ● and TFE ○ solvent systems**

$\pi \rightarrow \pi^*$ cotton effects corresponding to the two amide chromophores present in each repeating unit. The weak negative band, which was not detected in methanol[32], can be tentatively considered as resulting from contributions of $n \rightarrow \pi^*$ electronic transitions, this type of transition being known to absorb in the 220–230 nm region for monosubstituted amides[33] and to be solvent dependent. However, that band might result from the overlapping of larger cotton effects located down in the u.v. too. In any case, the similarity between the spectra of polymer I and of model compound II shows that the repeating units are not exciton coupled in agreement with the non-regular structure of the polymer chains. In MSA, c.d. spectra of compounds I and II are still similar though the positive band observed at 194 nm is much weaker for the polymer than for the model compound. For both, the change from TFE to MSA apparently results in a decrease in magnitude of the positive band and in a blue-shift of its maximum. Actually, c.d. changes caused by MSA are more complicated and depend on the amount of acid present in the mixture as evidenced in *Figure 5*. When adding increasing amounts of MSA in TFE at a fixed amide concentration, the positive band decreases drastically to become negative. The comparison with c.d. spectra in pure MSA (*Figure 4*) shows that the sign changes again for high τ values. The variations of ellipticity at 200 nm of the maximum of the positive c.d. band observed for model compound II in methanol[32] has been plotted too in *Figure 5*. In that alcohol, ellipticity still decreases in the range of increasing low τ values but the drop is more progressive than in TFE and no change in sign is observed for intermediate acid contents. Opposite effects, i.e. steeper drop and larger negative ellipticities, are observed for model compound II when sulphuric acid is used instead of MSA, in TFE as in methanol. Therefore, acid-induced optical activity changes depend not only on the acid but on the alcohol too.

Drastic c.d. changes caused by the addition of very small amounts of H_2SO_4 to a solution of camphorolactam in TFE have already been reported and have been assigned to protonation of the amide chromophore of that conformationally rigid molecule[34]. As polyamide I and model compound II are definitely flexible molecules and as both compounds behave similarly insofar as optical activity is concerned, we believe that no ordered macromolecular conformation nor order-to-disorder conformational transition is to be invoked to account for the acid-induced o.r.d and c.d. changes reported here for polyamide I. Therefore, it is concluded that the enormous c.d. changes caused by MSA and H_2SO_4 at low τ values primarily reflect protonation of the amide chromophores. So far, the literature dealing with protonation of polyamides has been essentially qualitative. This fact is due to the complexity of protonation phenomena, even for low *MW* compounds[35], and to the polyelectrolytic nature of the very weak polybases that are amide-containing polymers in strong acid media[36]. For polymer I, the quantitative interpretation of experimental data is still complicated by the presence of two different amide groups, whose base strengths are different[35], in repeating units. If our interpretation, which contrasts with the belief that spectral changes reflect conformational changes, is right, similar o.r.d. and c.d. changes should be found for other non-stereoordered amide-containing polymers and for other optically active model compounds. This point will be considered in detail in following papers.

ACKNOWLEDGEMENT

This work has been supported by the CNRS through its ATP 'Chiral Structures' program (Grant no 2665).

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