with those described in the Experimental Section. Chemical shift values obtained in the above manner on a P(HB-*co*-HV) sample containing 16 mol % HV are reported in Table V.

(28) See Doi et al. and Bluhm et al. in ref 9.

(29) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrometric Identification of Organic Compounds*, 4th ed.; John Wiley and Sons: New York, 1981; Chapter 5, pp 259–261 and references within.

(30) A detailed discussion concerning the metabolism of a carbon source to the various repeating units which were identified in the corresponding PHA is found in ref 16 and 17, above.

(31) A random comonomer sequence distribution for PHA copolyesters is not unprecedented; see ref 25 and 28.

(32) Studies by ^{1}H NMR on P([*R*]-HB) indicate a preference, in chloroform, for the gauche conformation related to the 2_1 helix of P([*R*]-HB) and P([*R*]-HV) observed in the solid state; see: Doi, Y.; Kunioka, M.; Nakamura, Y.; Soga, K. *Macromolecules* **1986**, *19*, 1274.

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(34) For an excellent recent review of macromolecules which contain long *n*-alkyl pendant groups, see: Plate, N. A.; Shibaev, V. P. *Comb-Shaped Polymers and Liquid Crystals* Plenum Press: New York, 1987; Chapters 1–3. See also: Plate, N. A.; Shibaev, V. P. *J. Polym. Sci., Macromol. Rev.* **1974**, *8*, 117.

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Photoresponsive Polymers. Photostimulated Aggregation–Disaggregation Changes and Photocontrol of Solubility in Azo-Modified Poly(glutamic acid)

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ABSTRACT: The photochromic properties of poly(L-glutamic acid) containing 21, 52, and 85 mol % azobenzene units in the side chains were investigated. In suitable conditions, depending on the azo content, the trans $\rightleftharpoons$ cis photoisomerization of the azobenzene units was accompanied by aggregation–disaggregation processes and precipitation–dissolution of the polymers. The phenomena were fully reversible and could be photoregulated by irradiating at the appropriate wavelength. The polymer solubility was studied as a function of the cis/trans isomeric composition of the azobenzene side chains. It was found to change as a sharp phase transition, the midpoint occurring at about a 50/50 cis/trans isomeric ratio. Findings are consistent with a molecular mechanism in which aggregation and precipitation processes occur through hydrophobic interactions and ordered stacking between the azobenzene moieties. Such interactions can be favored or inhibited depending on the trans $\rightleftharpoons$ cis photoisomerization of the azo units, thus causing the photoresponse effects.

Introduction

Polymers containing azobenzene moieties have recently attracted considerable interest, mainly because of their potential use as photoresponsive systems.[1-3] In particular conditions, in fact, the trans $\rightleftharpoons$ cis photoisomerization of the azo groups can be accompanied by reversible variations of the macromolecular conformation and the physical properties of the polymers. Interesting light-induced conformational changes were found to occur in azo polypeptides,[4-10] which exist in ordered conformations, such as α-helix and β-structure, and more closely approximate biological systems.

In preliminary papers, we have also reported the occurrence of photostimulated aggregation–disaggregation processes[11] and reversible variations of solubility induced by light.[12] The former phenomenon was observed in aged solutions of azo-modified poly(L-glutamic acid) containing about 20 mol % azobenzene units in the side chains. The latter was exhibited by an analogous azo polypeptide, having a much higher content of azobenzene groups. In order to have a complete and detailed picture, these photoresponse effects have been investigated in samples of azo-modified poly(L-glutamic acid) having various contents of azobenzene units in the side chains, in various solvent conditions, and at different wavelengths of the incident light.

The results obtained show that aggregation–disaggregation or precipitation–dissolution processes can be actually photoregulated by irradiating at the appropriate wavelength. the findings also provide a clear and well-fitting explanation of the molecular events that are responsible for the photoresponse effects described.

Experimental Section

Materials. Trifluoroethanol (TFE) and hexafluoro-2-propanol (HFP) were of spectroscopic grade. Trimethyl phosphate (TMP) was purified by fractioned distillation; its absorbance at 200 nm in a 1-cm cell was 0.8.[13]

***N*-Acetyl-α-(phenylazo)-L-glutamanilide (I).** *N*-Acetyl-γ-benzyl-L-glutamic acid (2.79 g, 10 mmol) was dissolved in chloroform (100 mL) and the solution cooled to 0 °C. *p*-Aminoazobenzene (1.97 g, 10 mmol) and dicyclohexylcarbodiimide (2.26 g, 11 mmol) were added in that order, and the mixture was stirred for 2 h at 0 °C and overnight at room temperature. The precipitated dicyclohexylurea was removed and the solution was washed with 5% $NaHCO_3$, 5% acetic acid, and water. After evaporation of the solvent, the product was crystallized from ethyl acetate/petroleum ether to give 3.2 g (7 mmol) of *N*-acetyl-γ-benzyl-*p*-(phenylazo)-L-glutamanilide.

Benzyl groups were removed by treating the above product (0.32 g, 0.70 mmol) with 0.1 N NaOH (8 mL) in dioxane (30 mL) for 1 h at room temperature. The solvent was evaporated, then water was added, and aqueous solution washed with ether and acedified to pH 4. Finally the oily product was extracted with ethyl acetate and crystallized by adding petroleum ether. Absorption spectra:

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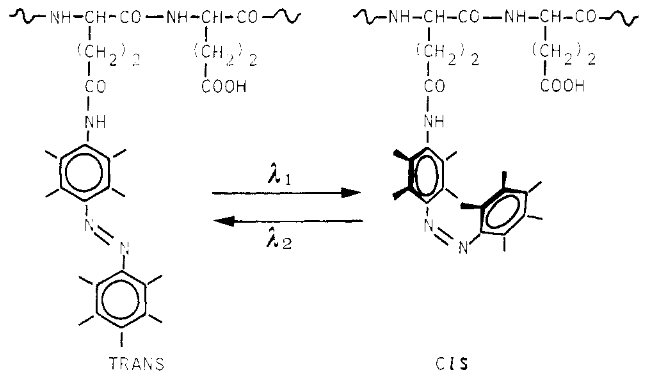
Scheme I



in TMP, λ_{max} = 355 nm, ϵ_{max} = 27400; in HFP, λ_{max} = 340 nm, ϵ_{max} = 23000.

Azo-modified polymers were obtained by reacting poly(L-glutamic acid) ($\bar{M}_v$ = 200000) with *p*-aminoazobenzene in the presence of dicyclohexylcarbodiimide and *N*-hydroxybenzotriazole, with the following procedure.

Poly(L-glutamic acid) (2.00 g; 15.5 mmol of COOH groups) was dissolved in 125 mL of anhydrous dimethylformamide (DMF). *p*-Aminoazobenzene (6.10 g; 31 mmol), *N*-hydroxybenzotriazole (4.20 g; 31 mmol), and dicyclohexylcarbodiimide (6.38 g; 31 mmol) were added to the stirred mixture. After 10 days at room temperature, acetic acid (2 mL) was added and the precipitated dicyclohexylurea was eliminated. The bulk of the DMF was evaporated under vacuum and the polymer recovered by precipitation with ether. Any unreacted azo reagent was removed by repeated dissolutions and precipitations. The yellow modified polymer that resulted was soluble in DMF and HFP and was found to contain 85 mol % azobenzene units. Poly(L-glutamates) containing 21 and 52 mol % azobenzene units were obtained with the same procedure, changing the reaction times.

The azo contents were determined by elemental analysis, NMR, and absorption spectra. It was assumed that the molar extinction coefficient of the model compound I was the same as of the corresponding azo-modified Glu residues in the polymers.[14,15]

Measurements. Solutions of azo compounds were prepared in red light and kept in the dark to ensure full trans configuration at the beginning of the experiment.

Irradiations were carried out at 25 °C with a 150-W halogen lamp, employing narrow-band interference filters from Balzer. Irradiation times of about 100–300 s were usually enough to attain the photostationary state.

Absorption and CD spectra were recorded on a UVIDEC 510 spectrophotometer and a JASCO J500A spectropolarimeter, respectively. Below 250 nm, CD data are expressed in terms of molar ellipticity [Θ], based on the mean residue weight. Above 250 nm the molar ellipticity [Θ′] is referred to one azo-Glu residue.

Results

Photochromism. Scheme I shows the typical photochromic behavior of azo-modified poly(Glu), associated with the trans ⇌ cis photoisomerization of the azobenzene units. At room temperature in the dark, all azobenzene units are in the more stable trans configuration, which is essentially planar and fully conjugated.[16] Irradiation gives rise to the skewed and less stable cis isomer, were the two phenyl rings are twisted about the C—N= bonds, for steric reasons.[17,18] As a consequence of the large difference in the electronic situation of the cis and trans configurations, the photoisomerization reaction is accompanied by large variations of the absorption spectra (Figure 1).

In HFP, the trans form shows an intense band with a peak at 338 nm, which is due to a π–π* transition, and a weak band at 430 nm, which corresponds to a n–π* transition. Formation of a cis isomer is revealed by a strong decrease of the 338-nm band together with its shifting toward higher energies. In the same time, the intensity of the 430-nm band increases.

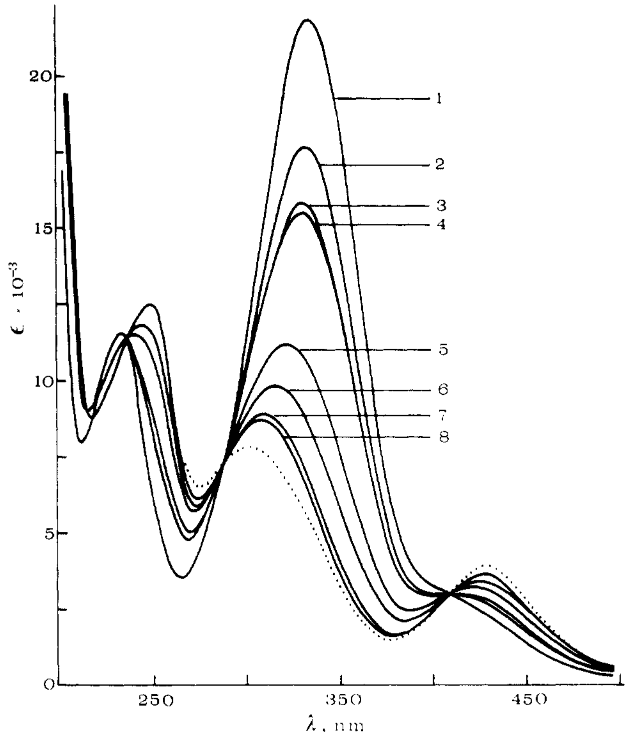


Figure 1. Poly(L-glutamic acid) containing 85 mol % azobenzene units in the side chains (c = 2.26 × 10^{-2} g/L in HFP, l = 1 cm). Absorption spectra relative to the photostationary states attained by irradiation at the indicated wavelengths: (1) dark-adapted sample; (2) 450 nm; (3) 407 nm; (4) 395 nm; (5) 381 nm; (6) 338 nm; (7) 372 nm; (8) 361 nm. (···) Calculated spectrum for the pure-cis isomer.[20] The molar extinction coefficient refers to one azo-Glu residue.

When solutions of azo compounds are irradiated at temperatures low enough to prevent thermal isomerization, a photostationary state is established. At this photosteady state, the relative composition of cis and trans isomers is predominantly determined by the extinction coefficients of the two isomers at the wavelength of the irradiating light.[19]

In order to investigate the dependence of the cis/trans composition on the wavelength of the incident light, both the azo-modified polypeptides and the model compound I, containing the same azo chromophore, were irradiated at various wavelengths, until the photostationary states were reached. We shall deal only with such states, and all isomer compositions will be those of the photostationary state attained with light at the wavelength indicated.

The results are reported in Table I. The absorbance variation between the trans and the cis isomer is maximum at 360 nm, so the isomerization was monitored at this wavelength. At any particular wavelength of the spectrum, the absorbance of a mixture of trans and cis isomers, where the overall concentration [trans] + [cis] is constant, is given by the eq 1,[20,21] where A_{st} is the absorbance of the sample

$$A_{st} = A_{trans}f_{trans} + A_{cis}f_{cis} \tag{1}$$

at the photostationary state, A_{trans} and A_{cis} are the absorbances of the pure-trans and -cis isomers, respectively, f_{trans} and f_{cis} their molar fractions, such that

$$f_{trans} + f_{cis} = 1 \tag{2}$$

On the basis of eq 1 and 2, the molar fractions of the trans and the cis isomers will be given by

$$f_{trans} = \frac{A_{st} - A_{cis}}{A_{trans} - A_{cis}}$$

$$f_{cis} = 1 - f_{trans}$$

Table I
85 mol % Azobenzene-Containing Poly(L-glutamic acid):[a] Trans/Cis Composition of Azobenzene Units at the Photostationary States Obtained by Irradiation at Various Wavelengths

		isomer comp	
λ_{irr}, nm	A_{360}[b]	f_{trans}, %	f_{cis}, %
dark	1.03	100	0
308	0.54	47	53
338	0.38	30	70
348	0.34	26	74
361	0.25	16	84
372	0.29	20	80
381	0.35	27	73
395	0.60	54	46
407	0.76	71	29
417	0.80	79	21
450	0.85	81	19

[a] HFP solution; $c = 2.36 \times 10^{-2}$ g/L; $l = 1$ cm. [b] Absorbance at the photostationary state, measured at 360 nm.

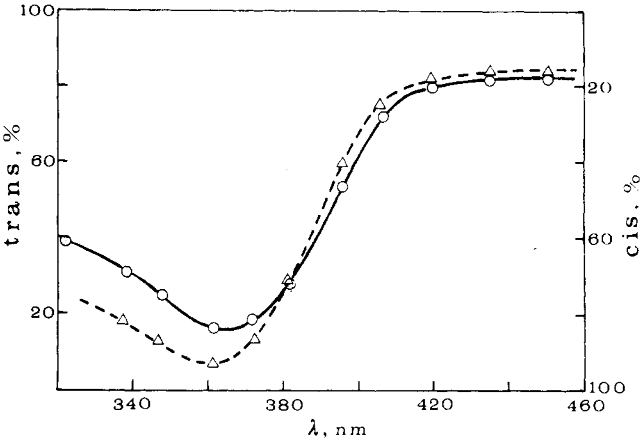


Figure 2. Trans/cis composition of azobenzene units at the photostationary state, as a function of irradiation wavelength, in HFP at room temperature: (—) 85 mol % azo-modified poly(L-glutamic acid); (- - -) low molecular weight compound I.

The absorbance of the 100% trans isomer, A_{trans}, corresponds to that of the sample kept in the dark, while the absorbance of the 100% cis isomer, A_{cis}, can be obtained by the absorption spectrum calculated with the method of Fischer[20] (Figure 1).

The cis isomer appears to have relatively little absorption in the region of the main absorption band of the trans isomer (Figure 1). For this reason the isomer composition is commonly estimated by assuming that the contribution of the cis isomer, A_{cis}, to the optical density in this wavelength region may be neglected.[22,23] In this case, the degree of trans-to-cis isomerization is substantially proportional to the relative decrease of the intensity of the main absorption maximum, A_{st}/A_{trans}. Estimation of f_{trans} and f_{cis} molar fractions, on the basis of the above assumption, leads to slightly higher numerical values for the trans isomer fraction of about 1–8%, depending on the irradiation wavelength.

Figure 2 shows the dependence of the cis/trans composition at the photostationary state as a function of the wavelength of the irradiating light. The behavior is quite similar for the polymers and the model compound.

High contents of cis isomer can be obtained by irradiating at $\lambda < 380$ nm, while high contents of trans isomer can be achieved by irradiating at $\lambda > 420$ nm. The photostationary state containing the maximum of cis content can be reached by irradiating at 361 nm. At this wavelength, the trans-to-cis photoconversion is nearly quantitative in the low molecular weight compound (95–97%), while it reaches 84% in the high polymers. For the polymers, apparently, a portion of the trans isomer is unable to isomerize to the cis form, probably due to the unfavorable environment.[24]

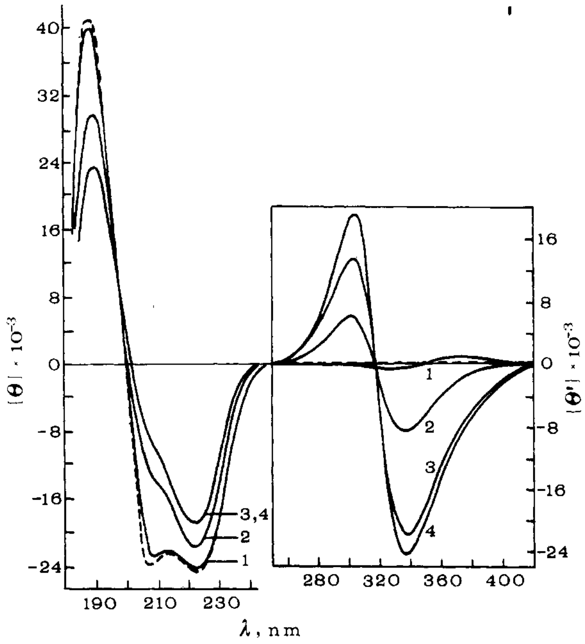


Figure 3. Poly(L-glutamic acid) containing 21 mol % azobenzene units. CD spectra in TMP/water = 50/50, recorded at various aging times: (1) freshly prepared solution; (2) 1-day aged; (3) 2-day aged; (4) 3-day aged solution; (—) dark-adapted samples; (- - -) irradiated at 361 nm, at any aging time.

In the dark, the back-isomerization from the cis to the trans form takes place according to first-order kinetics for both polymers and model, as previously reported.[14]

Light-Induced Aggregation–Disaggregation Processes. We have already reported in a preliminary paper[11] some CD data providing evidence that azo-modified poly(Glu) containing 21 mol % azobenzene units can undergo reversible aggregation–disaggregation processes upon exposure to light or dark conditions. Samples stored in the dark or irradiated at 450 nm (azo groups in the trans configuration) show variations of their CD spectra on aging in a TMP/water solution (Figure 3). The time dependence is characterized by the gradual appearance of an intense side-chain CD couplet together with a progressive distortion of the α-helix pattern, typical of those produced by aggregates of polypeptide chains.[25–27]

Irradiation at 361 nm (trans to cis isomerization) produces the full restoration of the initial CD spectra, indicating dissociation of the aggregates. The spectra revert again to the distorted ones by irradiating at 450 nm or by dark adaptation, thus confirming the reversibility of the light-induced effect.

An analogous photoresponse has been now observed in a polypeptide containing 52 mol % azobenzene units. In pure TMP, the CD spectrum of the dark-adapted sample shows the two negative bands at 222 and 208 nm typical of α-helical polypeptides. Addition of increasing amounts of TFE produces variations of the CD spectrum, which are characterized by red-shifting of the 222-nm band toward 225 nm and progressive flattening of the 208-nm band.

As we said above, these features of the spectra are usually observed in helical polypeptides[25–27] when aggregation phenomena occur and also in proteins when CD measurements are carried out on turbid solutions.[28,29] Actually, the main sources of these distortions are due to an absorption flattening effect and to the differential scattering of the left and right circularly polarized light

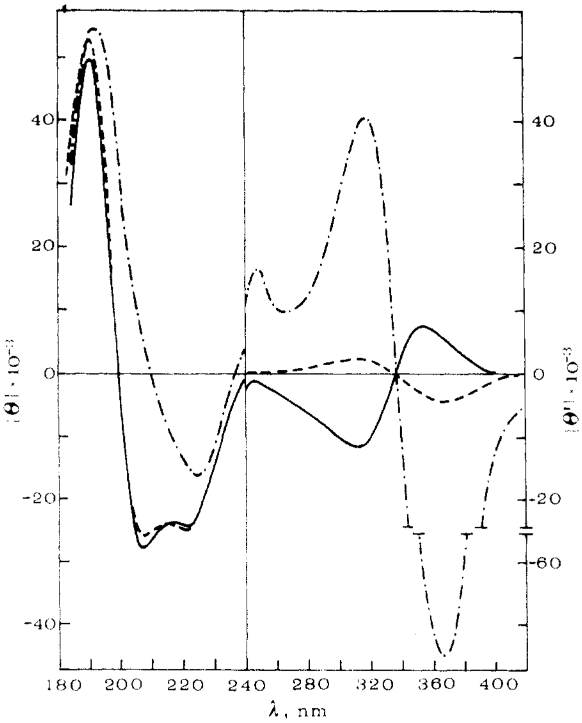


Figure 4. CD spectra of poly(L-glutamic acid) containing 85 mol % azobenzene units: (—) dark-adapted sample in pure HFP; (···) dark-adapted in HFP/water = 85/15, immediately after addition of water and before precipitation of the polymer; (- - -) redissolved polymer in HFP/water, after irradiation at 361 nm (see text).

produced by the presence of aggregates.[25,29]

The variation of the CD spectra produced by the addition of TFE to the 52% azo polypeptide must be associated with an aggregation process of the helical chains, analogously to that observed in the aged solutions of the 21 mol % azo polymer. Accordingly, light-scattering intensity increases on increasing TFE concentration and aging of the solutions. Formation of aggregated structures is also accompanied by hypochromism of the absorption spectra in the 340-nm region. In TMP/TFE = 60/40, the 52% azo polymer absorbs roughly 10% less than does the model compound I, in the same solvent and the same azo concentration. A hypochromic effect of the same order is observed in the aged solutions of the 21% azo polymer with respect to the freshly prepared samples.

Irradiation at 361 nm and the consequent trans-to-cis isomerization restore the typical α-helix profile at any TFE concentration. The photoisomerization itself of the azo units does not affect the CD spectrum in the peptide region, as can be observed in the freshly prepared solution (Figure 3) or in pure TMP. So the light effect cannot be masked by different contributions of the azo chromophore in the trans or cis configuration. The variation of the CD spectra upon irradiation can be well interpreted as resulting from the dissociation of the aggregates stimulated by light. Upon irradiation at 450 nm or dark adaptation (trans-to-cis back isomerization), the spectra revert again to the distorted ones. The photoresponse cycles can be repeated by UV irradiation and dark adaptation or by irradiating alternately at 360 and 450 nm.

Photomodulation of Solubility. Investigation of azo-modified poly(Glu) containing 85 mol % azobenzene units in the side chains has provided confirmation of the occurrence of aggregation–disaggregation processes induced by light, together with the possibility of photoregulating polymer solubility.

In HFP, the polypeptide stored in the dark (azo groups in the trans configuration) assumes the α-helix structure, as shown by the profile of the CD spectrum below 250 nm (Figure 4). A positive couplet of bands is also centered at 340 nm, in correspondence of the main absorption maximum of the azo chromophore in this solvent.

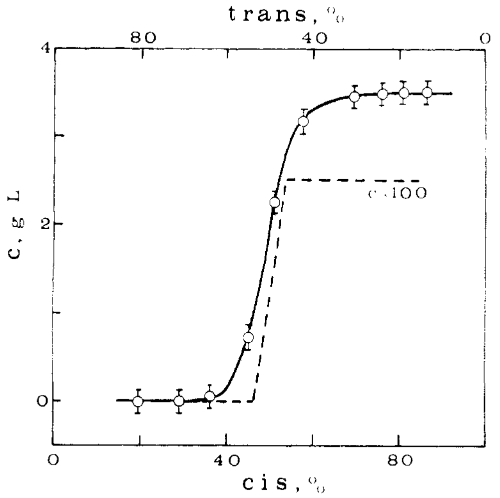


Figure 5. Variation of the solubility of azo-modified poly(L-glutamic acid) as a function of the cis/trans configuration of the azo side chains, at the room temperature: (—) 85 mol % azo polymer in HFP water = 85/15; (- - -) 52 mol % azo polymer in HFP/water = 80/20. The azo isomer composition in HFP/water solvent mixture was assumed to be the same as in pure HFP.

Addition of a small amount of water (15% vol) to the HFP solution stored in the dark causes, as a first step, formation of aggregates and then precipitation of the polymer. In fact, the CD spectrum recorded immediately after the addition of water (Figure 4) exhibits the typical distortion features in the peptide region and an intense couplet of bands, due to the azo side chains, the chirality of which is opposite to that observed in pure HFP. This step is followed quite soon by the precipitation of the polymer as a yellow material. The precipitation is total and quantitative, as can be seen by recording the absorption spectrum of the filtered colorless solvent.

Irradiation of the suspension for a few seconds at 361 nm causes the complete dissolution of the polymer. The obtained solution displays the same CD spectrum in the peptide region as the original one (Figure 4). Of course, the side-chain bands are not restored because the azobenzene units have the trans configuration in the dark-adapted sample, while they are mainly cis in the irradiated one.

Irradiation at 450 nm or dark adaptation of the solution makes the polymer precipitate again. In a HFP/water = 85/15 solvent mixture, the "precipitation–dissolution" cycles can be reversibly repeated by irradiation and dark adaptation or by irradiating at two different wavelengths. Only partial photosolubilization is obtained when the water concentration is higher than 15%.

In order to investigate the dependence of the polymer solubility on the cis/trans composition of the azobenzene side chains, irradiation experiments were carried out at various wavelengths of the incident light. The considerable amount of photodissolved polymer allowed its determination by evaporating the solutions obtained upon irradiation and weighing the dry residue. The results are illustrated in Figure 5.

The solubility of the 85 mol % azo-modified polymer as a function of the cis/trans ratio of azobenzene side chains is described by a sharp sigmoidal curve. This indicates that the process induced by light takes place like a conformational or phase transition. The polymer is fully insoluble when more than 60% azo groups are in the trans configuration. By contrast, the maximum amount of photosolubilization is achieved when 60% azo groups are in the cis configuration, then the solubility remains unaffected at higher values of cis content. The midpoint of the transition is in correspondence with a 50/50 trans/cis isomeric composition.

For the 52 mol % azo-modified polymer, a detailed investigation of solubility as a function of cis/trans ratio of the azo groups was not possible, because of the small amount of material which can be reversibly dissolved and precipitated upon irradiation. However, a solution of 2.5×10^{-2} g/L in HFP/water = 80/20 was fully precipitated by irradiating at 395 nm (46% cis), and it was fully redissolved by irradiating at 308 nm (53% cis) (Figure 5). This confirms the sharp variation of the polymer solubility within a narrow range of cis/trans compositions of the azo side chains.

Discussion

Polypeptides containing azobenzene units in the side chains were found to give rise to association and precipitation phenomena under suitable solvent conditions. These conditions appear to differ, depending on the azo content. For 21 mol % azo-modified poly(L-glutamic acid), association takes place in a TMP/water = 50/50 solvent mixture, on aging of the solutions. For 52 mol % azo-modified polymer, aggregation is observed when TFE is added to TMP solutions. Finally, the highly modified polymer containing 85 mol % azo groups precipitates on adding water to the HFP solution.

In all cases, association and precipitation processes take place when azobenzene units in the side chains are predominantly in the trans configuration but do not occur when azobenzene units are mainly in the cis configuration. Under suitable conditions, therefore, the trans $\rightleftharpoons$ cis photoisomerization of the azobenzene side chains is accompanied by "aggregation–disaggregation" processes among macromolecules or "precipitation–dissolution" of the polymer. The processes are reversible and can be photomodulated by irradiating at the appropriate wavelength.

The observed photoresponse effects could in principle be explained by considering the higher polar character of the cis form with respect to that of the trans form of the azo groups. Actually, in azobenzene, the dipole moment was reported to be 3.0–3.1 D for the cis isomer and 0–0.5 D for the trans isomer.[30,31] In the presence of water or polar solvent, therefore, the cis form should be more soluble than the trans form, so the trans–cis photoisomerization is expected to change the solubility of azo-modified polypeptides.

On the other hand, the variation of solubility as a function of the cis/trans ratio of azobenzene units is described by a sharp sigmoidal curve (Figure 5). This can hardly be explained considering only the different polarity of the two isomers. In fact, if the higher polarity of the cis form were the decisive factor that causes the dissolution, then the polymer solubility should gradually increase on increasing the cis content. In contrast, the sharpness of the curve is an indication that the system is highly cooperative and that the precipitation–dissolution process occurs as a phase or conformational transition.

The described photoresponse effects can be well interpreted on the basis of association among macromolecules, through hydrophobic interactions and stacking of azobenzene side chains. These interactions are favored when azobenzene moieties are in the planar, apolar trans configuration, so association and eventual precipitation occur. By contrast, hydrophobic interactions are inhibited when the azo units are in the cis configuration, which is severely distorted from planarity. In *cis*-azobenzene in the crystalline state, for instance, the two phenyl rings are rotated by 53–56° about the C—N bond, relative to a planar N=N—phenyl arrangement.[17,18] So aggregates are disrupted upon trans-to-cis photoisomerization and polymer dissolution occurs.

Hypochromism in the main absorption region of the azo chromophore was found to accompany formation of aggregates. This is a confirmation that the aggregate structure involves interactions between the azo moieties, packed close together in a parallel stacked array. Interactions between azo groups are also consistent with the side-chain CD bands which gradually appear when association progresses (Figures 3 and 4). These bands, due to the exciton splitting of the π–π^* electronic transition of the azo chromophore, have unusual intensity and their sign is opposite with respect to that observed in pure solvent.[9,14] Actually, in the absence of association, the couplet should be originated by side-chain interactions along the helical polypeptide chain. In the presence of association, it should be originated by intermolecular interactions. Analogous side-chain CD bands with the same sign are also observed when azo polypeptides adopt β-structures.[7,10]

We can conclude that the primary photochemical reaction is the trans $\rightleftharpoons$ cis photoisomerization of the azobenzene units. However, the key factor responsible for the photostimulated variations of solubility in azo-modified polypeptides is the association–dissociation process through hydrophobic interactions and ordered stacking between the azobenzene moieties. This process occurs as a cooperative phase or conformational transition, thus amplifying the photoresponse effect.

Partial variations of solubility induced by light were found to occur also in polystyrene with azobenzene pendant groups in cyclohexane solution.[32] The sense of the photoresponse was opposite to that observed in polypeptides, so the solubility decreased on trans-to-cis photoisomerization. A different mechanism was proposed in this case.[33]

The described system can find potential applications in devices which can be photochemically modulated. The findings of the work may be also relevant to the molecular mechanisms responsible for photoregulated biological processes. Indeed, a photoinduced aggregation–disaggregation process has been recently reported in human immunoglobulin labeled with an azobenzene reagent.[34] Moreover, several studies on naturally occurring photoreceptors have provided evidence of changes in aggregation of protein matrices upon photoexcitation of the attached photochromic moiety.[35,36]

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Registry No. I, 117229-42-2.

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Thermotropic Liquid Crystalline Poly(ester β-sulfide)s Based on Twin Hexamethylene-Spaced *p*-Oxybenzoyl Diads

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ABSTRACT: A series of poly(ester β-sulfide)s, 6S*n*, has been prepared by reacting the mesogenic hexamethylene bis[4-[[4-(acryloyloxy)benzoyl]oxy]benzoate] (1) with α,ω-alkanedithiols with a different number *n* of methylene units (*n* = 2–10). All of the polymers exhibit a nematic phase whose stability depends on the length of the dithiol segment. The nematic phases are enantiotropic with the only exception being that of the last term of the series, for which monotropic character has been detected. Onset and isotropization temperatures of the mesophase show a pronounced even–odd alternation that also holds for the isotropization entropy. A detailed study of the dependence of thermal properties upon the molecular weight is reported and indications are provided on their practical independence of the molecular weight at $\overline{\mathrm{DP}}_n \geqslant 4$–5.

Introduction

Polymers in which rigid anisotropic moieties and flexible units are incorporated along the main chain backbone can exhibit liquid crystalline behavior in the melt.[1,2] The mesogenic units, which normally contain aromatic structures, introduce both limited flexibility and anisotropic interactions. However, as the mesogenic groups form part of the main chain, the polymer molecule must adopt a configurational packing whose features define the structure, the symmetry, and the stability of the mesophase. The strong overlap between the polymeric and the mesomorphic properties of the single mesogens leads to large intra- and intermolecular interactions affecting not only the rigid but also the flexible part of the repeating units in semiflexible systems.[3,4]

At the molecular level, the conformationally flexible segments can propagate intramolecularly, via the pattern of rotational states, the orientational correlation from a rigid group to the successive one. In turn, the intermolecular ordering of rigid groups, originated by the orientational and eventually positional anisotropic potential, may impose specific constraints on the flexible spacers, thus altering the statistical weight of their configurations established in the isotropic phase.[5–7] Consequently, the overall mesophase properties depend on the critical interplay between the order of the mesogenic units and the conformational changes induced by the local environment on the flexible spacer. They may be extremely sensitive to even subtle structural modifications on both the rigid and the flexible components of the repeat units.

With the objective of gaining a better insight into the control exerted by the structural factors on the onset and stability of the liquid crystalline state, a systematic investigation[8–14] was undertaken concerning the thermotropic behavior of different series of functional liquid crystalline semiflexible polyesters. Among them a series of poly(ester β-sulfide)s of general structure I was prepared by reacting mesogenic diacrylates with α,ω-alkanedithiols. Generally,

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