Polyelectrolytes Carrying Pendant (Cyanobiphenylyl)oxy Mesogenic Groups. Preparation, Characterization, and pH-Dependent Behavior in Aqueous Solution

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ABSTRACT: Side-chain liquid crystalline polyelectrolytes containing terminal (cyanobiphenylyl)oxy moieties were obtained through hydrolysis of the corresponding poly(maleic anhydride-*co*-alkyl vinyl ether)s with spacer lengths of 6–12 methylene groups. All polymers display a liquid crystalline phase. The transition temperatures are lower for the more rigid poly(maleic anhydride-*co*-alkyl vinyl ether)s. The enthalpy gain associated with the phase transition decreases with increasing rigidity of the polymeric backbone and with decreasing spacer lengths. In aqueous solution all polyelectrolytes have two distinct apparent pK_a values, 3.3 and 6.5, indicative for strong nearest neighbor interactions within a maleic acid moiety. At neutral pH a blue shift of the absorbance maximum is observed which increases with increasing spacer length. Above pH 8 the blue shift decreases, indicating a conformational transition of the polyelectrolytes from more compact microdomains to a more extended chain conformation.

Introduction

A large number of studies have been dedicated to polymers that can form hydrophobic microdomains in aqueous solution.[1–6] The repeating unit of these polymers resembles an amphiphile, and the microdomains have properties similar to those of surfactant micelles. They can solubilize water-insoluble compounds like arenes and alkanes. Polysoaps, like alternating copolymers of maleic acid and alkyl vinyl ethers, form a particular class of microdomain-forming polymers. With increasing degree of deprotonation, α, polysoaps can undergo a conformational transition from a more compact, microdomain conformation to an extended hydrated conformation similar to that of strong polyelectrolytes. The balance between the electrostatic repulsion between the charged groups on the polyelectrolyte backbone and the hydrophobic interaction between the aliphatic side chains determines the polysoap conformation. With aliphatic side chains containing 10 or more carbon atoms, the compact conformation is retained over the entire range of α as a result of dominating hydrophobic interactions. For side chains between butyl and decyl, a change in conformation is observed depending on α, while shorter chains show no conformational transition at all.[7]

The microdomain environment has been probed using fluorescence techniques, such as excimer formation, medium sensitivity of emission, and fluorescence quenching.[8–10] The fluorescence characteristics of dansyl groups covalently bound to copolymers of maleic anhydride and alkyl vinyl ether have been used to investigate the microenvironment and conformational transitions of these polymers in aqueous solution.[11] Also pyrene-labeled polysoaps have been reported in the literature for fluorescence probing.[12–15]

Polysoaps with biphenyl groups attached to the alkyl chains provide new compounds of which the microdomains can be intrinsically probed.[16] In the present study, poly(maleic acid-*co*-alkyl vinyl ether)s bearing (cyanobiphenylyl)oxy groups were prepared for this purpose. The polyelectrolytes were synthesized through hydrolysis of the corresponding, alternating maleic anhydride copolymer in an aqueous THF solution.[17,18] The (cyanobiphenylyl)oxy moieties are distributed regularly along the polyelectrolyte chain, and the observation of a spectral shift in UV or fluorescence spectra upon varying the solution pH can provide information on the microdomain structure. Besides the hydrophobic interactions between the side chains, the (cyanobiphenylyl)oxy groups induce an extra stabilization of the formed aggregates by π–π stacking interactions between the mesogens.[19,20]

Furthermore, the presence of (cyanobiphenylyl)oxy moieties may introduce anisotropic ordering, both in thermotropic[21] and in lyotropic[22,23] systems. In aqueous solution, this may result in very interesting water-soluble polymers forming highly ordered microdomains. The excimer-forming ability of the (cyanobiphenylyl)oxy mesogens gives additional information on orientational ordering in the liquid crystalline phase.[16]

The spacer length of the alkyl chain connecting the mesogen with the polymer backbone can relatively easily be varied, making the side chains more or less hydrophobic and influencing the microdomain formation.

These properties make the newly synthesized compounds also very attractive for a systematic investigation of the effects of varying charge density and hydrophobicity of the polyelectrolyte on the conformational changes in the presence of oppositely charged amphiphiles.[7,8,24,25]

Experimental Section

Synthesis. The polyelectrolytes were synthesized as outlined in Scheme 1. *n*-[(4-Cyano-4′-biphenylyl)oxy]alkyl vinyl ethers were synthesized as described before.[26–28]

Poly(maleic anhydride-*co*-*n*-[(4-cyano-4′-biphenylyl)oxy]alkyl vinyl ether)s (I-*n*). Dry benzene (5–10 mL) was added to a mixture of equimolar amounts of *n*-[(4-cyano-4′-biphenylyl)oxy]alkyl vinyl ether and freshly sublimated maleic anhydride (1–5 mmol). To the resulting mixture was added 0.1 mol % of azobis(isobutyronitrile) (AIBN) dissolved in dry benzene. The polymerizations were performed in sealed glass flasks under a nitrogen atmosphere at 60 °C for at least 24 h. After completion, the solvent was evaporated under reduced

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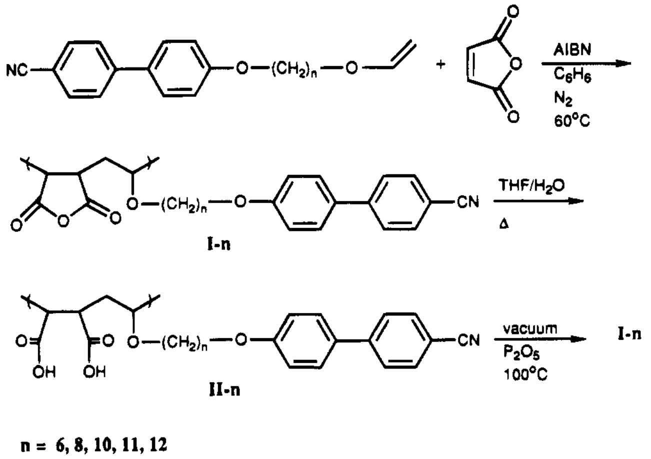
Scheme 1



pressure. The product was used in the hydrolysis reaction without further purification.

Poly(maleic acid-*co*-*n*-[(4-cyano-4′-biphenylyl)oxy]alkyl vinyl ether)s (II-*n*). **I-*n*** was dissolved in a mixture of freshly distilled THF and water and refluxed until the anhydride was completely hydrolyzed. The solvent was evaporated under reduced pressure and the residue was subsequently stirred in CH_2Cl_2. The precipitate was filtered and dried in vacuo. For further purification, it was sometimes necessary to redissolve the product in THF, evaporate the solvent, stir the residue in CH_2Cl_2, and filter the precipitate.

^{1}H NMR (DMSO-d_6): δ 1.2, 1.6 ($2n - 4$ H, $(CH_2)_{n-2}$), 2.8 (2 H, *CH*COOH), 3.3 (2 H, OCH_2), 3.8 (3 H, CH_2OPh and CHO), 6.9 (2 aromatic H, *o* to alkoxy), 7.5 (2 aromatic H, *m* to alkoxy), 7.7 (4 H, *o* and *m* to CN), 12.2 (2 H, COOH). FTIR (KBr): ν_{OH} 3500–2500, ν_{CH} 2930, 2855, ν_{CN} 2226, $\nu_{C=O}$ 1733 cm^{-1}. Anal. Calcd for **II-6**: C, 65.92; H, 6.42; N, 3.08. Found: C, 65.83; H, 6.06; N, 2.89. Anal. Calcd for **II-8**: C, 65.83; H, 6.96; N, 2.84. Found: C, 65.41; H, 6.44; N, 2.61. Anal. Calcd for **II-10**: C, 67.60; H, 7.32; N, 2.72. Found: C, 67.55; H, 7.01; N, 2.49. Anal. Calcd for **II-11**: C, 67.85; H, 7.52; N, 2.64. Found: C, 67.62; H, 7.19; N, 2.44. Anal. Calcd for **II-12**: C, 67.86; H, 7.72; N, 2.55. Found: C, 67.74; H, 7.23; N, 2.37.

Poly(maleic anhydride-*co*-*n*-[(4-cyano-4′-biphenylyl)oxy]alkyl vinyl ether)s (I-*n*). **II-*n*** was dried in vacuo at 100 °C over P_2O_5 for 7 days to give **I-*n***.

^{1}H NMR (DMSO-d_6): δ 1.2, 1.6 ($2n - 4$ H, $(CH_2)_{n-2}$), 3.3 (4 H, OCH_2 and CHCO), 3.8 (3 H, CH_2OPh and CHO), 6.9 (2 aromatic H, *o* to alkoxy), 7.5 (2 aromatic H, *m* to alkoxy), 7.7 (4 H, *o* and *m* to CN). FTIR (KBr): ν_{CH} 2929, 2856, ν_{CN} 2225, $\nu_{O=COC=O}$ 1861, 1780 cm^{-1}.

GPC measurements of **I-*n*** show a degree of polymerization of at least 250.

Methods. ^{1}H NMR (200 MHz) spectra were recorded on a Bruker AC200 spectrometer. FTIR spectra were recorded on a BioRad FTS-7 spectrometer. A Perkin-Elmer DSC-7 differential scanning calorimeter was used to determine the thermal transition enthalpies and temperatures, which are reported as the maxima and minima of their endothermic or exothermic peaks, respectively. In all cases, heating and cooling rates were 10 °C/min and the samples were stored at 80 °C for 15 min before scanning to obtain identical thermal histories for all compounds. Polarization microscopy was performed using an Olympus BH-2 microscope equipped with a Mettler FP82HT hot stage and an FP80HT temperature controller.

The molecular weights (M_w) of the polymers were determined by gel permeation chromatography (GPC; Waters, column, HR 4E + HR 5E; eluent, THF + 5% (m/m) acetic acid) equipped with an Applied Biosystems 759A absorbance detector set at 297 nm. The molecular weights were calculated with the use of a polystyrene calibration curve.

For the determination of the apparent pK_a values, solutions of 5×10^{-4} mol of repeating unit of **II-*n*** per liter were prepared in a 5 mM KCl solution in ultrapure water at pH 12. Titrations of the polymer samples were performed with a 0.1 M HCl solution in a thermostated vessel at 24.5 ± 0.5 °C. The pK_a values were determined using a known literature procedure.[29]

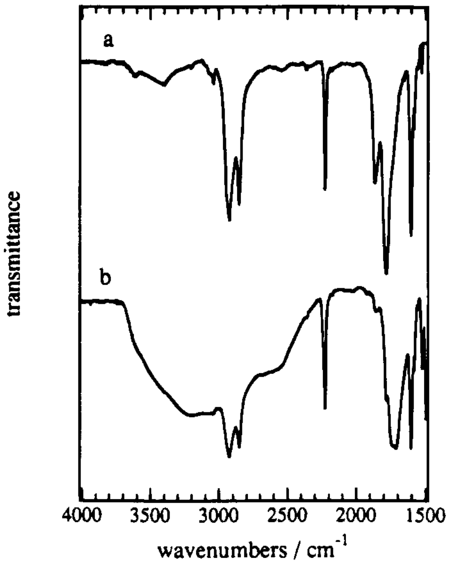


Figure 1. FTIR spectra of compounds **I-12** (a) and **II-12** (b).

UV spectra were recorded on a Beckman DU-7 spectrophotometer. All polyelectrolytes were dissolved at pH 7, and spectra were recorded after addition of aliquots of diluted HCl or NaOH.

Results and Discussion

Synthesis. The synthesis of the polymers is outlined in Scheme 1. The alkyl vinyl ether monomers were synthesized according to a literature procedure.[26–28] The poly(maleic anhydride-*co*-alkyl vinyl ether)s were synthesized by radical copolymerization of the alkyl vinyl ether monomers with maleic anhydride using AIBN as initiator. The radical polymerization of alkyl vinyl ethers with maleic anhydride is known to give perfectly alternating copolymers.[30,31]

Recently, the partial hydrolysis of polyacrylates bearing (cyanobiphenylyl)oxy units by use of NaOH was reported.[32] The acrylate ester bond was hydrolyzed, yielding a polyelectrolyte with a random distribution of (cyanobiphenylyl)oxy and acidic groups. Hydrolysis of **I-*n*** with dilute hydroxide at elevated temperatures resulted in the hydrolysis of the cyano moiety to the amide as was shown in the FTIR spectrum by the disappearance of the CN stretching vibration at 2226 cm^{-1}. Milder hydrolysis of **I-*n*** in a neutral aqueous THF solution gave **II-*n***.

As can be seen in Figure 1, the FTIR spectra clearly show the formation of the maleic acid moiety, without the loss of the CN stretch vibration. The symmetric and antisymmetric stretching bands typical for an anhydride at 1861 and 1780 cm^{-1} completely disappeared and the C=O stretching band characteristic for a carboxyl group at 1733 cm^{-1} appeared, showing the completion of the hydrolysis reaction.[33,34] The degree of polymerization was found to be at least 250. Comparable GPC chromatograms were obtained for **I-*n*** before hydrolysis and for **I-*n*** prepared by dehydration of **II-*n***, indicating that hydrolysis and dehydration do not influence the degree of polymerization. Both elemental analyses and NMR results confirm that the two comonomers are present in a 1:1 ratio.

Liquid Crystalline Properties. The thermotropic phase transition temperatures of the polymers were

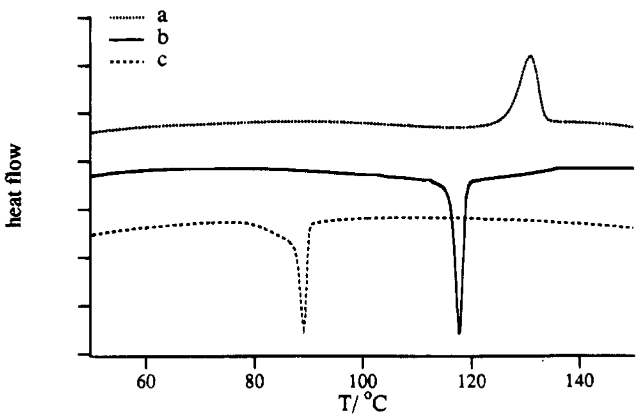


Figure 2. DSC thermograms of compound **II-11**: (a) second heating scan; (b) second cooling scan; (c) cooling scan after heating at 210 °C.

Table 1. Liquid Crystalline to Isotropic Phase Transitions for Compounds I-*n* (°C) and Their Corresponding Enthalpy Changes (in kJ/mol of Repeating Units)

spacer length	polarization microscopy lc → i	DSC lc → i	ΔH
6	95	82	0.3
8	120	116	0.5
10	102	112	2.0
11	110	110	2.0
12	117	116	3.1

Table 2. Liquid Crystalline to Isotropic Phase Transitions for Compounds II-*n* (°C) and Their Corresponding Enthalpy Changes (in kJ/mol of Repeating Units)

spacer length	polarization microscopy lc → i	DSC lc → i	ΔH
6	100	105	0.5
		128	0.3
8	125	132	1.5
10	121	127	2.2
11	127	131	2.5
12	158	151	4.4

investigated by hot stage polarization microscopy and DSC. All polymers **I-*n*** and **II-*n*** display a reversible liquid crystalline to isotropic phase transition by both DSC and polarization microscopy, except for compounds **I-6** and **II-6**, for which no transition was observed in the cooling trace of the DSC. The textures observed by polarization microscopy indicate smectic mesophases for both series of polymers.

The isotropization temperatures for compounds **I-*n*** are lower than for compounds **II-*n***. The polymer backbone influences the isotropization temperatures as a result of incomplete decoupling of the backbone and mesogenic moieties.[35] Isotropization temperatures generally increase with increasing backbone flexibility.[36,37] Compounds **I-*n*** have maleic anhydride units in the backbone, making the backbone more rigid than in compounds **II-*n***. This rigidity hampers the interactions between the mesogens, making the liquid crystalline state relatively less stable and lowering the isotropization temperature for **I-*n***.

The enthalpy gain upon isotropization is lower for polymers **I-*n***. Since the more rigid backbone of **I-*n*** restricts the motions of the mesogens, ordering of these mesogens is less than in the more flexible polymers **II-*n***. This results in a lower enthalpy for isotropization for the more rigid **I-*n*** polymers.

With increasing spacer length, the enthalpy gain increases as is usual for liquid crystalline monomers and polymers.[21,37-42] Compared to the values for homopolymers of alkyl vinyl ethers with (cyanobiphenylyl)oxy units, the enthalpy gain is lowered when these monomers are copolymerized with maleic anhydride and hydrolyzed to the maleic acid copolymers.[40-42] This implies a lesser extent of ordering for **I-*n*** and **II-*n*** as compared to the homopolymers, which can be attributed to changes in the backbone flexibility and the relative dilution of the mesogenic units of **I-*n*** and **II-*n***.

Polymer molecular weights can influence phase transition temperatures; therefore differences in isotropization temperatures as a result of molecular weight differences cannot be completely excluded.[39,40] The molecular weight distribution can also influence the thermal properties of side-chain liquid crystalline polymers.[43] It is reported that the isotropization temperature and the glass transition temperature of poly(vinyl ether)s are both strongly dependent on the molecular weights of the polymers.[44] However, a strong molecular weight dependence is usually only seen for degrees of polymerization of less than 20.[41,45] The degrees of polymerization of **I-*n*** were found to be at least 250, so no influence of the molecular weights is expected on the thermotropic properties.

DSC measurements showed a decrease in isotropization temperature for **II-*n*** after heating at 210 °C (Figure 2). FTIR investigations of the heated samples showed the partial reappearance of the anhydride stretch vibrations. This indicates that at higher temperatures the polyelectrolytes are partially dehydrated. However, the maleic anhydride copolymers **I-*n*** also showed a decrease in isotropization temperature after heating at 210 °C. This lowering in the isotropization temperature might be caused by a partial degradation of the polymers. Another possibility is the formation of anhydride cross-links within the same or between different polymeric backbones.

As the polymers were isolated in their glass state, no crystal to liquid crystalline phase transitions were observed. Also, we were not able to detect a T_g between −50 and +210 °C for all polymers. One possibility is that the T_g's of polymers **I-*n*** and **II-*n*** lie in the same temperature range as the liquid crystalline to isotropic phase transitions. It is known from the literature that poly(maleic anhydride-*co*-alkyl vinyl ether)s with octyl and decyl side chains have T_g's of respectively 120 and 104 °C.[33]

It is also known that as the spacer length is increased, the heat capacity change associated with the glass transition becomes smaller.[38] For our polymers the minimum spacer length, $n = 6$, might already be too long to observe the change in heat capacity.

The kind of mesophase formed also influences the T_g. The T_g of poly(biphenylylmethacrylate)s could only be observed if the polymer exhibited a nematic phase whereas for the smectic polymers the change in specific heat capacity at the glass transition is too low to be detected by DSC.[35] The low change in heat capacity is probably caused by the restricted motions of the polymeric backbone due to the lamellar smectic structure of the mesogenic side chains. This might give an indication for the formation of smectic mesophases by **I-*n*** and **II-*n***, resulting in a low specific heat capacity change upon cooling into the glass state.

The glass transition is also known to be highly dependent on the polymer molecular weight,[33] usually only showing a dependence for degrees of polymerization of 12 and lower.[40] However, no reports were found which mention the effect of the molecular weight on the change in the specific heat capacity.

pK_a Values. For all spacer lengths the titration curves of solutions of **II-*n*** in 5 mM KCl solution in water are the same, implying that there is no influence of the chain length on the pK_a values. All polyelectrolytes exhibit two apparent pK_a values of 3.3 ± 0.3 and 6.5 ± 0.1. These pK_a values are in accordance with those reported for the poly(maleic acid-*co* alkyl vinyl ether)s with ethyl, butyl, and hexyl chains. For these polysoaps, pK_a values of 3.8 and 6.6 were found.[46,47]

The fact that two pK_a values are observed implies that the two maleic acid moieties within a monomeric unit mainly have strong nearest neighbor interactions. Recently, it was found by Kawaguchi et al.,[48] by resolving FTIR spectra, that upon increasing the degree of deprotonation, α, of poly(isobutylene-*co*-maleic acid), dissociation of the first acid group instantaneously leads to the formation of a hydrogen bond with the nearest acid group. Up to $\alpha = 0.5$ all ionized COO^- groups are immediately hydrogen bonded, and above $\alpha = 0.5$ the $COO^- \cdots HOOC$ pairs are destroyed. At low α values the solubility of polymers **II-*n*** in water decrease, and below pH 7 the slow formation of microcrystals is observed.[49]

Formation of Microdomains. In an organic solvent like THF the UV spectra of **II-*n*** display a maximum absorption at 297 nm, which corresponds to the absorption of monomeric, nonstacked (cyanobiphenylyl)oxy moieties.[50] In aqueous solution at low pH a blue shift is observed for all polyelectrolytes. According to the molecular exciton model proposed by McRae and Kasha,[51] the blue shift from the monomer band is indicative of linear chromophore aggregation with their transition moments parallel to each other and ordered perpendicular to the stacking direction (so-called H-aggregates). The wavelength shift depends on the degree of aggregation, which is determined by the mutual orientation and the aggregation number of the chromophores. The observation of a blue shift is indicative for the formation of ordered microdomains in water. The microdomains are stabilized by hydrophobic interactions between the side chains and additionally by $\pi-\pi$ interactions between the (cyanobiphenylyl)oxy units.

The absorption maxima of compounds **II-*n*** are dependent on the pH. As the pH increases, the absorption maxima shift from 270 nm for **II-12** and 278 nm for **II-6** at pH 3.4 to about 286 nm at pH 13.4 for all the polyelectrolytes studied.[49] This final value corresponds to the absorption maximum observed for alkyltrimethylammonium surfactants with a (cyanobiphenylyl)oxy moiety in aqueous solutions.[50] At high pH no aggregation is observed as a result of dominating electrostatic interactions on the polymeric backbones, resulting in the loss of stacking of the (cyanobiphenylyl)oxy moieties. For polyelectrolyte **II-6** the absorption maximum starts to shift to higher wavelengths at pH 8, indicating the beginning of the transition from more compact microdomains to a more loosely ordered, extended chain conformation at higher pH. The transition to an extended chain occurs at higher pH values with the elongation of the spacer connecting the mesogen and the polymeric backbone. As can be seen in Figure 3, the pH to reach the midpoint of the transition to a more extended conformation increases with increasing spacer length.

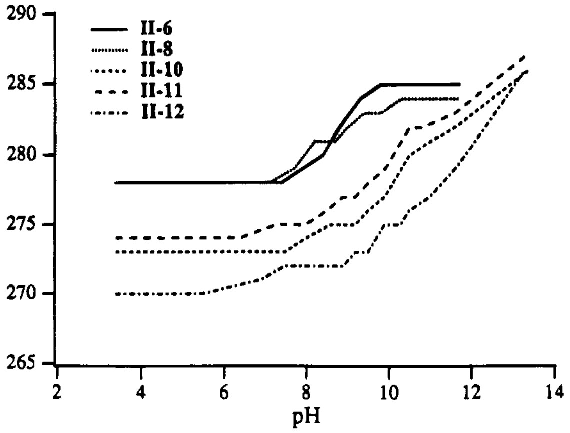


Figure 3. Absorption maxima of **II-*n*** as a function of the pH.

This effect of the spacer length on the stabilization of the microdomains is also seen at neutral pH where the absorption maximum for **II-12** exhibits the largest blue shift as a result of the strongest interaction between the (cyanobiphenylyl)oxy units. The mesogens in this polymer have the largest amount of freedom to obtain the most favorable mutual $\pi-\pi$ interaction.

Conclusion

A new and convenient method to synthesize side-chain liquid crystalline polyelectrolytes with a perfectly alternating distribution of the mesogenic moieties has been developed.

All polymers show liquid crystalline behavior, the isotropization temperatures being higher for the more flexible **II-*n*** polymers. The enthalpy changes associated with the phase transition are higher for **II-*n*** than for **I-*n*** and increase with increasing spacer length. No glass transitions were observed, probably due to the low change in the specific heat capacity at this transition, caused by the rigidity of the backbones and enhanced by strong mesogen interactions in the liquid crystalline phase.

The behavior of the polyelectrolytes in aqueous solution as a function of the degree of deprotonation can be studied intrinsically with UV measurements and titration experiments. The pK_a values agree well with values reported in the literature for analogous polyelectrolytes. UV measurements show the formation of microdomains at pH values below 8 by the observed blue shift of the absorption maximum. The polyelectrolyte bearing the longest spacer is the most hydrophobic polyelectrolyte and because of its most flexible spacer allows for the strongest $\pi-\pi$ interactions between the (cyanobiphenylyl)oxy units. This is confirmed by an increase of the blue shift with an increase of spacer length of the polyelectrolytes.

At pH values above 8, the poly(maleic acid-*co*-*n*-[(4-cyano-4′-biphenylyl)oxy]alkyl vinyl ethers)s show a transformation from the more compact globular conformation to a more extended chain conformation. The pH value at which this transition starts increases with increasing spacer length.

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