

Hypochromism of poly(2-vinylpyridine), poly(2-vinylnaphthalene) and polyacenaphthylene

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The u.v. hypochromy of poly(2-vinylpyridine) of different degree of isotacticity, atactic poly(2-vinylnaphthalene) and polyacenaphthylene in relation to 2-ethylpyridine, 2-ethylnaphthalene and acenaphthene, respectively, was evaluated. In the case of poly(2-vinylpyridine) the hypochromic effect was greater for an isotactic-rich sample (8.2%) than for an atactic one (4.8%). The decrease in absorption intensity of polymers containing naphthalene chromophores was compensated by broadening of the u.v. bands and the hypochromy was relatively small: 4.7% for poly(2-vinylnaphthalene) and 4.3% for polyacenaphthylene. © 1997 Elsevier Science Ltd.

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INTRODUCTION

Interactions leading to a decrease in u.v.-vis. absorption intensity of a polymer in comparison with that of a base unit model compound are well known for many biological polymers^{1,2}. Less information is available, however, for synthetic vinyl polymers. The effect of hypochromy can be evaluated as

$$H = (1 - f_p/f_m)100\% \quad (1)$$

where H is the hypochromism in %, f_p and f_m are the oscillator strengths of the polymer and the base unit model, or as

$$H' = (1 - f_{i-p}/f_{a-p})100\% \quad (2)$$

where H' is the hypochromism in %, f_{i-p} and f_{a-p} are the oscillator strengths of the isotactic and atactic polymer, respectively.

The oscillator strength is given by the equation³

$$f = 4.319 \times 10^{-9} \int \epsilon(\bar{\nu})d\bar{\nu} \quad (3)$$

in which ϵ is the molar extinction coefficient (per chromophore) in $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$, $\bar{\nu}$ is the wavenumber in cm^{-1} .

So far the u.v. spectrum of polystyrene (PS) has been studied extensively⁴⁻⁷ and the hypochromy of atactic PS was found to be small ($\sim 2\%$)⁵ whereas it is of appreciable value in the case of isotactic polymer (up to 10%)^{4,6,7}. Substantial hypochromy comparable to that of native DNA was found in poly(*N*-vinylcarbazole) (~ 25 and $\sim 35\%$ for 1L_b and 1L_a bands, respectively)⁸⁻¹² and in vinyl polymers carrying large side groups: poly(9-vinylphenanthrene), poly(3-vinylpyrene), poly(9-vinylacridine) (10, 17 and 18% for 1L_b + 1L_a bands, respectively)⁸.

The similarity of the u.v. spectra of poly(1-vinylnaphthalene) (P1VN) and poly(2-vinylnaphthalene)

(P2VN) and their respective low-molecular weight models has been shown in several reports¹³⁻¹⁸. Semerak and Frank¹⁹ concluded that the absorbance spectra of P1VN and P2VN are red shifted about 4 nm and display 15% less absorbance at the maximum relative to 1- and 2-isopropylnaphthalene, respectively. Polyacenaphthylene (PACN) is another polymer containing the naphthalene chromophore but bound to the polymer main chain at two adjacent carbon atoms. This polymer has been extensively studied by Springer and coworkers who reported the u.v. spectrum of PACN in MTHF ($\epsilon_{\text{max}} = 5200 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ at $33\,700 \text{ cm}^{-1}$)²⁰ and found a red displacement of ca 8 nm as compared to acenaphthene (AcN)²¹. The values of ϵ_{max} of AcN reported in the literature²²⁻²⁴ vary from 7100 to $6300 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ (in various solvents). David *et al.*²⁵ presented the spectrum of PACN with $\epsilon_{\text{max}} \cong 7000 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$. No diminishing of absorption intensity of PACN as compared to AcN was reported by Okamoto and coworkers⁸.

The spectra of polyvinylpyridines in CHCl_3 were studied by Noel and Monnerie²⁶ who determined the specific extinction coefficients (in $\text{dm}^3 \text{ g}^{-1} \text{ cm}^{-1}$) and compared them with those of ethylpyridines. The intensity reduction of 15% was found for ϵ_{max} at λ_{max} for poly(2-vinylpyridine) (P2VP) in relation to 2-ethylpyridine. P2VP is interesting for our investigations since the isotactic polymer (3/1 helix, identity period 6.7 Å) can be prepared according to Natta²⁷. It has been shown in our previous paper⁷ that the hypochromism of PS increases with increasing content of isotactic material in the sample. In this study we examined the spectra of atactic and 69% isotactic P2VP.

An analysis of the u.v. spectra of P2VN, PACN and P2VP and the evaluation of hypochromy in these polymers is the aim of this paper.

EXPERIMENTAL

Materials

Atactic poly(2-vinylnaphthalene) ($\bar{M}_w = 4.58 \times 10^5 \text{ g mol}^{-1}$) and 69% isotactic poly(2-vinylpyridine) ($\bar{M}_w = 1.5 \times 10^5 \text{ g mol}^{-1}$) were kindly supplied by Prof. W. Klöpffer (C.A.U. GmbH, Frankfurt) and Prof. G. O. R. Alberda von Ekenstein (State University of Groningen), respectively. Atactic poly(2-vinylpyridine) ($\bar{M}_w = 2 \times 10^5 \text{ g mol}^{-1}$) was purchased from Polyscience Inc. and purified by precipitation from the THF solutions with hexane. Polyacenaphthylene was obtained from Polyscience Inc. The sample was dissolved in benzene and precipitated in excess methanol. Its weight-average molar mass (\bar{M}_w) determined in toluene at 25°C using the relationship²⁸: $[\eta] = 8.38 \times 10^{-3} \bar{M}_w^{0.65}$ was $4 \times 10^5 \text{ g mol}^{-1}$. Acenaphthene (Aldrich) was purified by triple crystallization from ethanol. 2-Ethynaphthalene and 2-ethylpyridine purchased from Aldrich were Analar reagents. Chloroform, tetrahydrofuran and methanol, special grades for spectroscopy were used as solvents.

Measurements

Ultra-violet spectra of solutions were recorded with a Gilford Response II UV/VIS spectrophotometer.

RESULTS AND DISCUSSION

The u.v. spectra of atactic poly(2-vinylpyridine) (a-P2VP), 69% isotactic poly(2-vinylpyridine) (i-P2VP) and 2-ethylpyridine (2EtP) are shown in Figure 1. The spectra of atactic poly(2-vinylnaphthalene) (a-P2VN) and 2-ethynaphthalene (2EtN) as well as polyacenaphthylene (PAcN) and acenaphthene (AcN) are presented in Figures 2 and 3, respectively.

In general, the u.v. spectra of all the investigated polymers are similar to those of base unit models; it should be noticed, however, that

- the polymer absorption bands (1L_b , 1L_a) are shifted to the lower wavenumbers in comparison with those of the corresponding models (see Table 1),
- the vibrational structure of 1L_b and 1L_a bands of the polymers is more diffused,
- the absorption intensity of polymers in the range of 1L_b and 1L_a bands is lowered.

The changes in absorption intensity were evaluated by comparing the oscillator strengths given by equation (3).

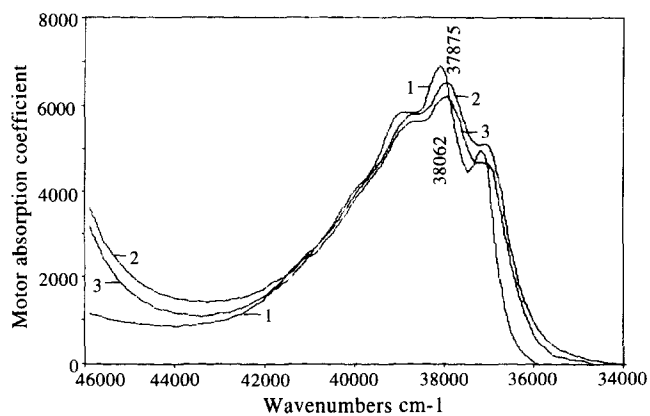


Figure 1 U.v. absorption spectra of 2EtP (1), a-P2VP (2) and 69% i-P2VP (3) in methanol solution

The integrated absorption intensity of the band, $\int \epsilon(\bar{\nu})d\bar{\nu}$, was calculated assuming that each band is a superposition of several Gaussian error functions of the form:

$$\epsilon = \epsilon_{\max}[-B(\bar{\nu} - \bar{\nu}_{\max})^2] \quad (4)$$

where ϵ is the molar extinction coefficient (in $\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) and $\bar{\nu}$ is the wavenumber (in cm^{-1}).

The hypochromisms H and H' in (%) were determined according to equations (1) and (2). The results of Gaussian band fittings are summarized in Table 2 and exemplary extinction curves are shown in Figures 4 and 5. The values $\bar{\nu}_{\max}$ of Gaussian sub-bands were found by considering the vibrational structure of the absorption bands. The number of Gaussian components was

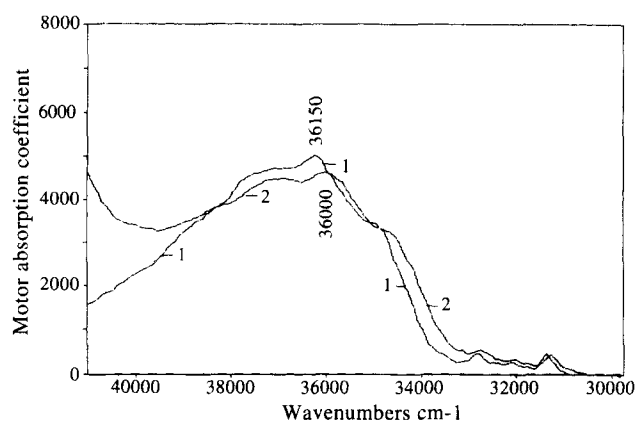


Figure 2 U.v. absorption spectra of 2EtN (1) and a-P2VN (2) in THF solution

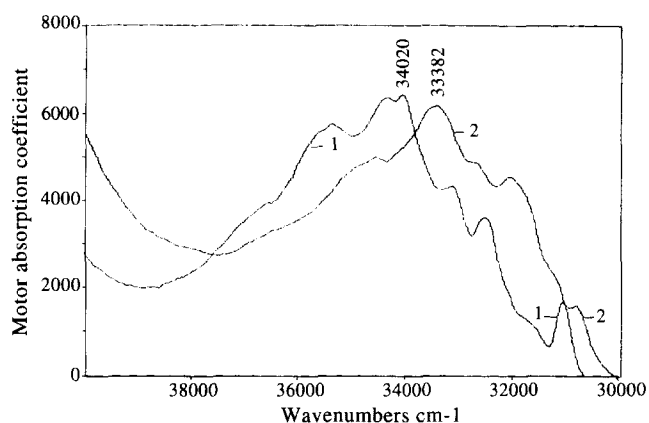


Figure 3 U.v. absorption spectra of AcN (1) and PAcN (2) in CHCl_3 solution

Table 1 Red shift of polymer absorption bands in comparison with base unit models^a

Polymer	Reference	Absorption band	Red shift $\Delta\bar{\nu}$ in cm^{-1}	Red shift $\Delta\lambda$ in nm
a-P2VP	2EtP	1L_b (max)	187	1.3
69% i-P2VP	2EtP	1L_b (max)	125	0.9
a-P2VN	2EtN	1L_a (max)	150	1.2
PAcN	AcN	1L_a (max)	638	5.6
PAcN	AcN	1L_b (0-0)	239	2.5

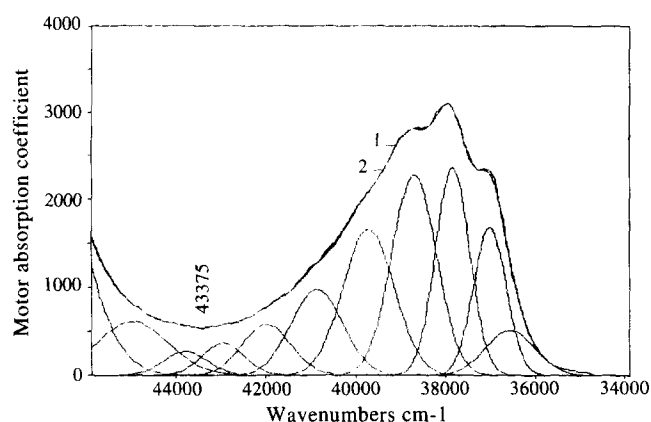
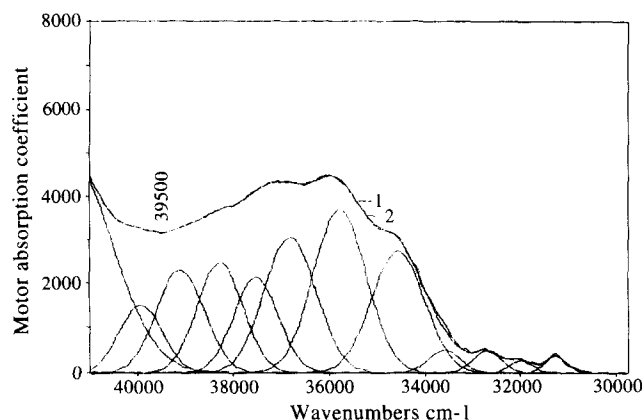
^a a-P2VP: atactic poly(2-vinylpyridine); 69% i-P2VP: sample containing 69% isotactic poly(2-vinylpyridine); 2EtP: 2-ethylpyridine; a-P2VN: atactic poly(2-vinylnaphthalene); 2EtN: 2-ethynaphthalene; PAcN: polyacenaphthylene; AcN: acenaphthene

Table 2 Experimental values of maximum extinction coefficient ϵ_{\max} , short wavelength minimum ν_{\min} and calculated oscillator strength f for absorption bands of poly(2-vinylpyridine), poly(2-vinylnaphthalene) and polyacenaphthylene and their low-molecular weight models^a

Polymer	Solvent	Error ^b	Number of Gaussian sub-bands	Absorption band	ϵ_{\max}	ν_{\min} (cm ⁻¹)	$f \times 10^2$
a-P2VP	CH ₃ OH	16	8	¹ L _b	3270	43 250	5.92
69%	CH ₃ OH	19	8	¹ L _b	3110	43 375	5.73
i-P2VP							
2EtP	CH ₃ OH	16	9	¹ L _b	3360	43 950	6.21
a-P2VN	THF	31	10	¹ L _a + ¹ L _b	4520	39 500	10.31
2EtN	THF	21	11	¹ L _a + ¹ L _b	5050	41 190	10.83
PACN	CHCl ₃	40	9	¹ L _a + ¹ L _b	6210	37 250	13.04
AcN	CHCl ₃	52	10	¹ L _a + ¹ L _b	6420	38 830	13.63

^a a-P2VP: atactic poly(2-vinylpyridine); 69% i-P2VP: sample containing 69% isotactic poly(2-vinylpyridine); 2EtP: 2-ethylpyridine; a-P2VN: atactic poly(2-vinylnaphthalene); 2EtN: 2-ethylnaphthalene; PACN: polyacenaphthylene; AcN: acenaphthene

^b Error of fittings determined as $\sqrt{(\epsilon_{\max} - \epsilon_{\text{fit}})^2/n}$, where ϵ_{\max} and ϵ_{fit} are the experimental and calculated molar absorption coefficients, respectively, and n is the number of measured extinction values

**Figure 4** U.v. absorption spectra of 69% i-P2VP in methanol solution resolved into Gaussian sub-bands; (1) experimental data, (2) spectrum calculated as a superposition of sub-bands**Figure 5** U.v. absorption spectra of a-P2VN in THF solution resolved into Gaussian sub-bands; (1) experimental data, (2) spectrum calculated as a superposition of sub-bands

dependent also on the position of short wavelength minimum, $\bar{\nu}_{\min}$ (indicated in Table 2) which value was close to the coordinate of the point of crossing of the two adjacent sub-bands (e.g. 8th and 9th Gaussian curves with $\bar{\nu}_{\max}$ of 42 929 and 43 770 cm⁻¹, respectively, for i-P2VP). The Gaussian sub-bands with $\bar{\nu}_{\max}$ lower than $\bar{\nu}_{\min}$ were assumed to belong to the absorption band of interest. In the case of a-P2VP and i-P2VP it was possible

to determine the integrated absorption intensity of ¹L_b band while for P2VN and PACN the overall intensity of ¹L_b and ¹L_a bands were calculated. The ¹L_b band of PACN and AcN is hidden under the ¹L_a band of PACN and AcN so that the only vibrational peak maxima could be evaluated. In the case of P2VN the ¹L_b band is more shifted to the longer wavelengths but it was difficult to attribute the fourth Gaussian curve (with $\bar{\nu}_{\max} = 33 585$ cm⁻¹) to one of the mentioned two bands. The experimental and fitted extinction curves are sufficiently superimposable; the values of errors calculated as $\sqrt{(\epsilon_{\max} - \epsilon_{\text{fit}})^2/n}$, where ϵ_{\max} and ϵ_{fit} are the experimental and calculated molar absorption coefficients, respectively, and n is the number of measured extinction values, are included in Table 2. The oscillator strength of u.v. transitions calculated according to equation (3) as well as the hypochromicities H and H' determined by the use of equations (1) and (2) are summarized in Tables 2 and 3.

CONCLUSIONS

The effect of hypochromy has been found in all the investigated polymers. The values of hypochromy calculated here and in our previous study⁷ (determined with the aid of Gaussian sub-band fittings taking into account the assumptions given above) allow us to compare the hypochromy in a series of polymers listed in Table 3. It follows from theoretical considerations² that interactions leading to the effect of hypochromy

Table 3 Experimental hypochromism H and H' of u.v. absorption bands of poly(2-vinylpyridine), poly(2-vinylnaphthalene) and polyacenaphthylene^a

Polymer	Solvent	Absorption band	Basic unit model	H in %	H' in %
a-P2VP	CH ₃ OH	¹ L _b	2EtP	4.79	
69%	CH ₃ OH	¹ L _b	2EtP	8.21	3.25
i-P2VP					
a-P2VN	THF	¹ L _a + ¹ L _b	2EtN	4.73	
PACN	CHCl ₃	¹ L _a + ¹ L _b	AcN	4.33	

^a a-P2VP: atactic poly(2-vinylpyridine); 69% i-P2VP: sample containing 69% isotactic poly(2-vinylpyridine); 2EtP: 2-ethylpyridine; a-P2VN: atactic poly(2-vinylnaphthalene); 2EtN: 2-ethylnaphthalene; PACN: polyacenaphthylene; AcN: acenaphthene
 H and H' are calculated in relation to a base unit model and an atactic polymer, respectively (cf. equations (1) and (2))

increase with (i) the increasing strength of absorption, (ii) the decreasing distance of chromophores and (iii) are the largest for the parallel arrangement of chromophores.

In the case of poly(2-vinylpyridine) the effect is more pronounced for the isotactic-rich sample. The same trend was observed for polystyrene samples of different isotacticity investigated in our previous paper (H was 2.05%, 5.27% and 7.55% for atactic, 60% isotactic and 99% isotactic sample, respectively)⁷. It was also found that the hypochromism H' of 69% i-P2VP and 60% i-PS is comparable (3.25 and 3.29%, respectively). It is known that 3/1 helices with similar repeat distances are formed in solid isotactic PS²⁹ and isotactic P2VP, and it is accepted that partial retention of the helical arrangement is preserved in i-PS solutions. The similar values of H' for these two polymers allow us to suppose that the partial helical ordering is also possible in i-P2VP solutions. The larger values of hypochromy H of P2VP in comparison with PS can be related to the higher oscillator strengths of u.v. transitions in P2VP than in PS.

The hypochromicities of atactic P2VN and PAcN are comparable and rather small in spite of the fact that the oscillator strengths of these polymers are about twice as large than those of P2VP. It seems reasonable to assume that the arrangement of naphthalene chromophores is far from the parallel one. It is clear in this case that the broadening of the bands compensates for the decrease in absorption intensity.

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