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HYPOCHROMISM OF VINYLPOLYMERS WITH LARGE PENDANT π-ELECTRON SYSTEMS

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The absorption spectra of vinylpolymers with large pendant π-electron systems show the hypochromism, change in the structure of the ^1B_b or ^1B_a band, and lower (or higher)-frequency shift in comparison with the spectra of the monomeric models. These arise from some electronic interactions between neighboring chromophores in a polymer chain.

Recently, the emission spectra of vinylpolymers with large pendant π-electron systems have been extensively investigated in expectation of informations about behaviors of excited and conformational structures in solution as well as in solid film.[1-5] The absorption spectra of these vinylpolymers have scarcely been investigated in detail in comparison with the spectra of the monomeric model compounds. It is, nevertheless, assumed that their absorption spectra are almost the same as those of monomeric models, and that there is no interaction between pendant chromophores in a polymer chain in the ground state.[2,3]

It is well known that the spectral properties of biological macromolecules such as nucleic acids and proteins differ considerably from those of the monomeric chromophores. For instance, the optical density of these polymers decreases when the molecules are transformed from a random coiled conformation (whose spectral properties are similar to those of the monomeric chromophore) to a helical one.[6,7] The decrease in the absorption intensity, or the hypochromism, is attributed to exciton interaction and dispersion-force interaction in a polymer with an ordered structure.[8,9] So far as we know, polystyrene (PSt) is the only synthetic aromatic vinylpolymer which has been studied hitherto concerning the hypochromism.[10]

In the present study we investigated the absorption spectra of a series of vinylpolymers with large pendant π-electron systems in order to obtain some informations about interaction between neighboring chromophores in a polymer chain.

The materials studied are listed in Table 1. PVCz, PVPh, PVPy, and PVAc have the large pendant π-electron systems connected directly to the skeletal chains of the polymers. In PCzEVE and PPhEVE the carbazyl and phenanthryl groups are connected far apart from the skeletal chains by $-CH_2-CH_2-O-$ bonds. The ethyl compounds were used as monomeric model compounds of the aromatic vinylpolymers.

UV absorption spectra in solution were measured by a Shimazu UV-200 spectrophotometer at 20°C, and are shown in Figs. 1-4. The spectral data are listed in Table 2 and 3. The spectral properties of PVCz or PVPy to be presented below were the same for every sample (DP > 20), irrespective of the method of polymerization.

Table 1. The materials studied

Material	Abbreviation	Preparation	Degree of polym.(DP)
N-ethylcarbazole	ECz		
1,4-bis(N-carbazolyl)butane	DCzB		
1,3-bis(N-carbazolyl)propane	DCzP		
N-vinylcarbazole oligomer	VCzOlig I	HCl in acetonitrile	5
N-vinylcarbazole oligomer	VCzOlig II	HCl in acetonitrile	10
Poly-N-vinylcarbazole	PVCz	radical, cation and Ziegler	>100
Poly-N-carbazolylethylvinylether	PCzEVE	cation (ref.11)	33
9-Ethylphenanthrene	EPh		
Poly-9-vinylphenanthrene	PVPh	radical (ref.12)	18
Poly-9-phenanthrylethylvinylether	PPhEVE	cation (ref.11)	90
3-Ethylpyrene	EPy		
Poly-3-vinylpyrene	PVPy	radical and cation (ref.13)	20 and 200
9-Ethylacridine	EAc		
Poly-9-vinylacridine	PVAc	living anion (ref.14)	100

In a series of carbazoles, the absorption bands of PVCz, VCzOlig I and II are shifted to higher wavenumbers by 100 - 400 cm^{-1} as compared with those of ECz, although such a shift is not observed in the case of PCzEVE and DCzB.[15)] The shift in the case of VCzOlig I is rather larger than that in the case of PVCz and VCzOlig II. The higher-frequency shift in the case of PVCz and VCzOlig I and II is very interesting, because the absorption bands of the other aromatic vinylpolymers are shifted oppositely to lower wavenumbers as compared with those of the monomeric models. As for the absorption bands structure, the ^1B_a band of PVCz differs significantly from that of the low molecular model compounds, although no difference in the ^1L_b, ^1L_a and ^1B_b bands is observed among these compounds. The ^1B_a band of VCzOlig II is rather similar to that of PVCz and that of VCzOlig I is intermediate between those of PVCz and ECz. On the other hand, the ^1B_a band of PCzEVE is rather similar to that of ECz, in spite of relatively high degree of polymerization. The absorption intensity, or oscillator strength, of PVCz decreases to 53-76 % of that of ECz. The decrease in the absorption intensity of VCzOlig II is large, but it is small in the case of VCzOlig I. The absorption intensity of PCzEVE decreases to about 90 % of that of ECz. This is much smaller than the decrease in the case of PVCz with a similar molecular weight.

These results were obtained in good solvents for PVCz such as ethylenechloride and tetrahydrofuran (THF). In poor solvents, PVCz shows larger decrease in the absorption intensity. For instance, the absorption intensity in the mixed solvent of THF-cyclohexane (5/3 in volume ratio) decreases to 95 % (in the ^1L_a and ^1B_b bands) or 90 % (in the ^1B_a band) of that in THF. Such a decrease in the intensity is not observed in the case of PCzEVE.

In a series of phenanthrenes, the absorption bands of PVPh are shifted to lower wavenumbers by 300 and 600 cm^{-1} in the ^1L_b and ^1L_a bands, respectively, as compared with those of EPh. The lower-frequency shifts of the ^1L_b and ^1L_a bands of PPhEVE are 50-100 cm^{-1} and 200-300 cm^{-1}, respectively. These are much smaller than the shifts in the case of PVPh, in spite of the high degree of polymerization of PPhEVE. The ^1B_b absorption band differs among PVPh, PPhEVE, and EPh in the manner similar to the case of the ^1B_a bands of PVCz, PCzEVE, and ECz. The absorption intensity of PVPh decreases to 83-91 % of that of EPh while such a decrease is not

Table 2. Absorption data for vinylpolymers with large pendant π-electron systems and their low molecular model compounds. Absorption maxima[a)] are given in cm^{-1}, and molar (mole of chromophore) extinction coefficients[b)] (parenthesized) are given in 100 M^{-1} cm^{-1}.

ECz	28840(41.2)	30090(36.4)	33860(154)	37910(224)	42070(430)	43070(360)	
DCzB	28900(44.0)	30170(36.5)	33900(156)	38020(216)	42110(473)	43160(400)	
DCzP	29000(40.8)	30230(34.9)	34010(153)	38170(198)	42070(453)	43070(391)	
VCzOlig I	29160(31.1)	30350(30.4)	34070(118)	38340(147)	42340(350)	43380(362)	
VCzOlig II	29100(33.9)	30260(29.1)	33990(98.4)	38280(123)	42100(309)*	43380(366)	
PVCz	29100(31.4)	30260(26.5)	33900(88.3)	38280(115)	42000(250)*	43540(304)	
PCzEVE	28890(36.2)	30100(31.9)	33820(116)	37990(164)	42070(322)	43100(311)	
EPh	28570(4.03)	29310(2.60)	29960(4.03)	30660(2.68)	31400(2.92)	33450(103)	
PVPh	28270(2.78)	29000(2.14)*	29650(5.34)	30300(2.72)*	31000(4.60)*	32860(82)	
PPhEVE	28470(3.86)	29200(2.41)	29870(3.92)	30550(2.55)	31350(3.10)	33170(104)	
EPh	34840(94.0)	35970(127)	36970(165)	39140(542)	40320(4.40)*		
PVPh	34190(78.0)	35400(96.0)*	36700(160)*	39840(361)	—		
PPhEVE	34540(93.0)	35780(143)	37000(196)*	39370(470)	—		
EPy	26580(8.32)	27210(4.20)	27400(4.08)*	27800(8.47)*	29090(406)	30530(265)	31910(113)
PVPy	26440(6.43)	27100(10)*	—	—	28670(201)	30190(206)	31450(106)
EPy	33300(49)*	36140(503)	37590(255)	39060(121)	40980(1320)	42550(566)	
PVPy	32790(48)*	35820(250)	37240(175)	38840(116)*	40870(366)	42190(385)	
EAc	25970(42.6)	27870(96.5)	28430(73.5)	29220(47.5)	39110(1610)	40160(730)*	
PVAc	25510(31.3)	27610(56.1)	—	—	38460(246)*	40780(448)	

Solvent: Carbazole and phenanthrene series, ethylenechloride; pyrene series, THF; acridine series, chloroform containing 1 % ethanol. *) absorption shoulder.

a) with an error of about ± 20 cm^{-1}. b) with an error of about 2 %.

Table 3. Oscillator strengths (f)

Material	^1L_b	^1L_a	^1B_b	^1B_a	Total
ECz	0.046	0.118	0.208	0.72**	1.09
DCzB	0.046(1.00)	0.115(0.98)	0.189(0.91)	0.77(1.08)**	1.12(1.03)
DCzP	0.044(0.96)	0.116(0.98)	0.179(0.86)	0.73(1.02)**	1.07(0.99)
VCzOlig I	0.042(0.91)	0.109(0.92)	0.135(0.65)	0.65(0.91)**	0.94(0.86)
VCzOlig II	0.038(0.83)	0.089(0.75)	0.122(0.59)	0.66(0.91)**	0.91(0.83)
PVCz	0.035(0.76)	0.081(0.69)	0.110(0.53)	0.49(0.69)**	0.72(0.66)
PCzEVE	0.043(0.93)	0.104(0.88)	0.173(0.83)	0.63(0.87)**	0.95(0.87)
EPh	0.0043	0.23	0.80		1.04
PVPh	0.0039(0.91)	0.21(0.90)	0.67(0.84)		0.87(0.84)
PPhEVE	0.0041(0.97)	0.24(1.03)	0.76(0.95)		1.00(0.97)
EPy		0.35*	0.37	1.02	1.63
PVPy		0.29(0.83)*	0.28(0.76)	0.64(0.64)	1.21(0.74)
EAc		0.148	1.43		1.58
PVAc		0.122(0.82)	0.83(0.59)		0.95(0.60)
α-Ethylnaphthalene		0.120*			
Poly-α-vinylnaphthalene		0.121(0.99)*			
Acenaphthene		0.124*			
Polyacenaphthylene		0.126(1.02)*			

$f = 4.32 \times 10^{-9} \int_{\sigma_1}^{\sigma_2} \varepsilon(\sigma)\, d\sigma$, where σ_1, and σ_2 are effective wave number limits.

The numerical values parenthesized are the relative oscillator strengths compared with the values of the monomeric model compounds. The errors in the values of f are of the order of a few per cent.

*) ^1L_b + ^1L_a **) σ_2 = 45000 cm^{-1}.

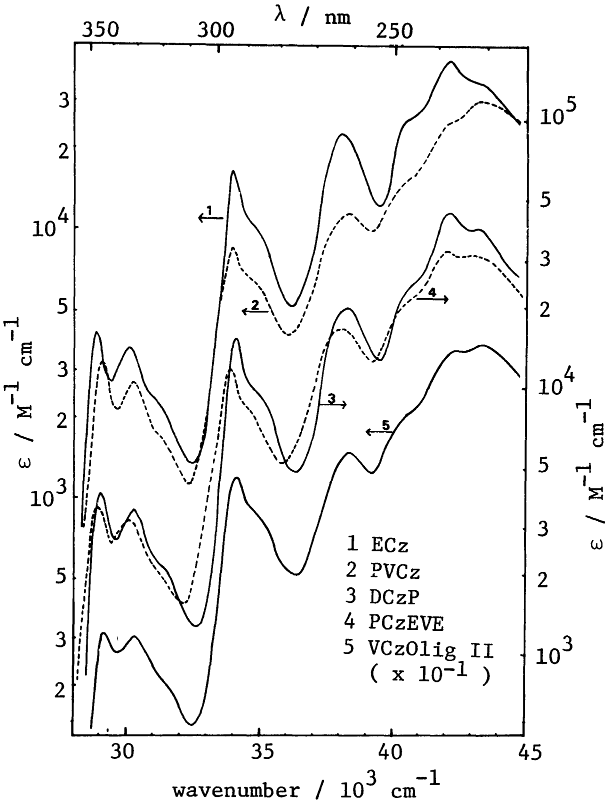

Fig. 1. Absorption spectra of PVCz and its related compounds in ethylenechloride.

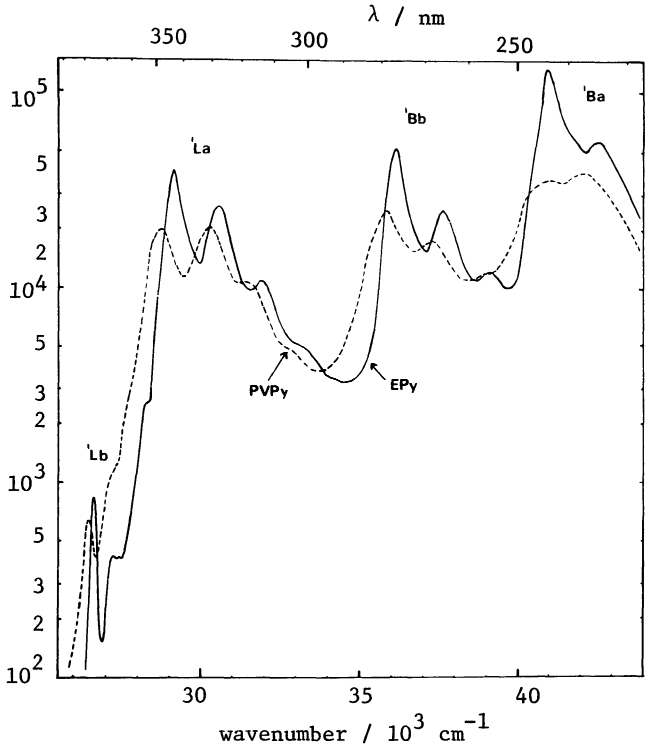

Fig. 3. Absorption spectra of PVPy and EPy in THF.

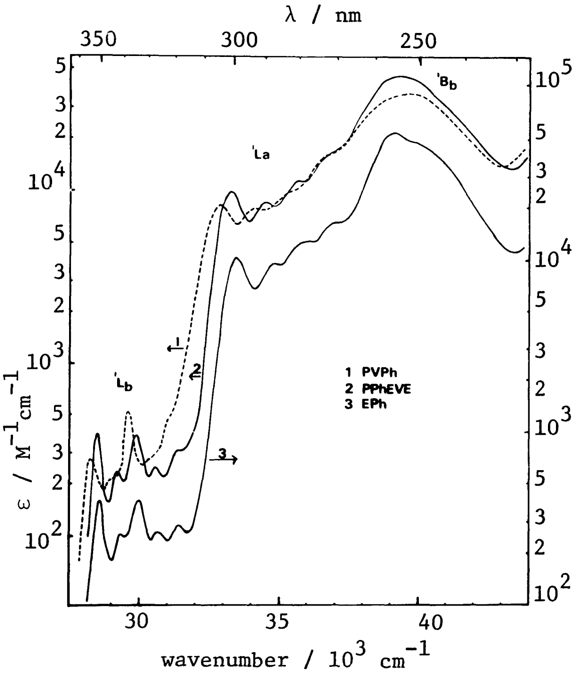

Fig. 2. Absorption spectra of PVPh, PPhEVE and EPh in ethylenechloride.

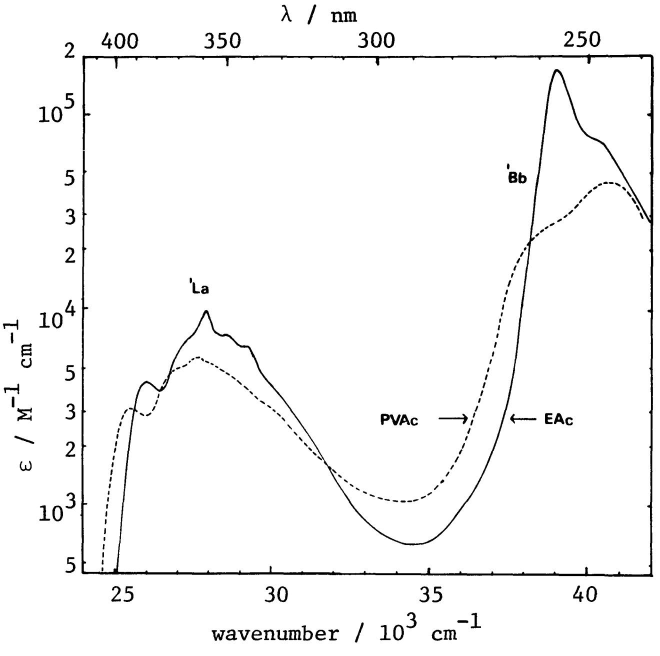

Fig. 4. Absorption spectra of PVAc and EAc in chloroform (1 % ethanol).

observed in the case of PPhEVE.

In the cases of PVPy and PVAc, there are similar differences of the spectral properties between the polymers and the monomeric models. That is, (1) the lower-frequency shift of the absorption bands by 110-460 cm^{-1} for PVPy and by 260-600 cm^{-1} for PVAc, (2) the change in the structure of the ^1B_a band for PVPy and of the ^1B_b band for PVAc, and (3) the decrease in the absorption intensity by factors of 1/2 - 2/3 (the decrease is in the orders; $^1B_a > {}^1B_b > {}^1L_a$ band).

On the other hand, in the case of the vinylpolymers with relatively small pendant π-electron systems prepared by radical polymerization (therefore, being atactic rather than isotactic), such as polyacenaphthylene, polyvinylnaphthalene and PSt, the absorption intensity is equal to that of the monomeric models, although the absorption bands are still shifted to lower wavenumbers in comparison with the spectra of the monomeric models.

The above-mentioned spectral properties of the vinylpolymers, such as the hypochromism, the change in the structure of the ^1B_b or ^1B_a band and the spectral shift, evidently arise from some electronic interactions between neighboring chromophores in a polymer chain. It should be noted that the interactions are appreciable only in the vinylpolymers (DP > 10) having large pendant π-electron systems connected directly to the skeletal chain, irrespective of the method of polymerization.

In the case of PSt, a vinylpolymer with a much small pendant π-electron system, the hypochromism is observed only in the isotactic polymer and is regarded as being due to the coulombic dipole-dipole interaction in neighboring chromophores because of the retention of the local helical structure in solution.[10)] In the case of the vinylpolymers with large pendant π-electron systems, the hypochromism is also probably due to the same interaction as reported both on the biological polymers and on PSt. It seems, therefore, to be a proof that the vinylpolymers with large pendant π-electron systems connected directly to the skeletal chain, irrespective of the method of polymerization, have some ordered structure in solution. This is not unreasonable on the base of the following NMR results, although being inconsistent with the result from the viscosity measurements which indicate that the dilute solution conformation is a random coil.[16)]

From NMR spectra and X-ray diffraction, the structure of PVCz has been suggested as follows.[17-19)] In solid the polymer chain has isotactic 3/1 and syndiotactic 2/1 helix parts in a stereoblock manner. It seems to retain the rigid stereoblock structure even in solution. This structure appears to be fairly insensitive to the method of polymerization because of the large bulky substituent group. From the similar effect of the large bulky substituent group on the conformation, it is assumed that the other vinylpolymers with large π-electron systems connected directly to the skeletal chain may have some ordered structure in solution.[20)] On the other hand, in the case of PCzEVE and PPhEVE, the polymer chain probably take the flexible random coil conformation in solution, because the bulky substituent groups are connected far apart from the skeletal chain. This is supported by the fact that the NMR spectrum of PCzEVE does not show the unusual shift of one or more aromatic proton to 5 τ being characteristic to the rigid conformation of PVCz in solution,[17)] as is shown in Fig. 5.

At the present time, we cannot, however, exclude the possibility that some short-range interactions are also operative in these vinylpolymers because of the fairly short length between the nearest neighboring chromophores in a polymer chain.

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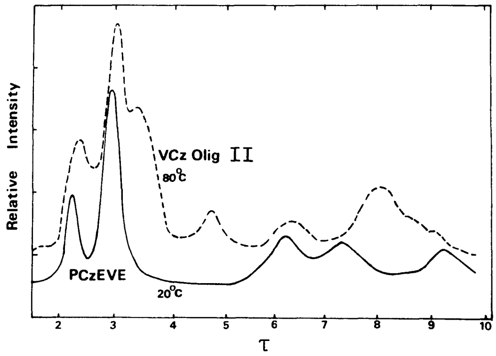

Fig. 5. 60-MHz MNR Spectra of PCzEVE and VCz Olig II in $CDCl_3$.

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19) D. J. Williams, ibid, 3, (1970).
20) This is supported by a private communication from professor H. Mikawa; The NMR spectrum of PVAc shows the unusual upfield shift of two aromatic proton to 4-5 τ and the existence of the methine proton with anomalous τ value (6.4).

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