Dyes and Pigments **15** (1991) 57–67

The Synthesis and Characterization of Polymerizable Azo-Naphthols for Use in Polymeric Materials

Khamis F. Shuhaibar & Harald Pasch

Products Department, Petroleum, Petrochemicals and Materials Division,
Kuwait Institute for Scientific Research, PO Box 24885, 13109—Safat—Kuwait

(Received 1 March 1990; accepted 9 April 1990)

ABSTRACT

Esterification of 1(2-nitrophenylazo)2,3-dihydroxynaphthalene and of 1(2-nitrophenylazo) 2,7-dihydroxynaphthalene and their methoxy and chloro derivatives with acryloyl chloride occurred at the 3- and 7-positions respectively and gave the acryloyloxyazo monomers in 40–63% yield. The acryloyloxy monomers were fully characterized by their infrared, ultraviolet and ^{1}H *and* ^{13}C *NMR spectra. Their copolymerization with styrene was studied.*

INTRODUCTION

The formation of colored coatings consisting of a polymeric matrix and a monomeric pigment has been known for a long time. Four classes of organic pigments are used, namely anthraquinones, phthalocyanines, quinacridones and azo compounds. These pigments usually are simply mixed with the polymeric matrix, thus remaining chemically independent in the final coating material. This may cause problems, such as separation of the dispersed pigment or migration of the pigment in the coated layer. In recent years efforts have been made to prepare dyes and pigments that have unsaturated groups in their molecules and can undergo copolymerization with different vinyl monomers. It was found that the polymers thus obtained had excellent properties.[1–4]

In this work, phenylazo-2-hydroxynaphthalenes containing unsaturated acrylate groups presented in two different positions in the naphthalene ring

Dyes and Pigments 0143-7208/90/$03·50

were synthesized and characterized. Their copolymerization with styrene was studied.

EXPERIMENTAL

Melting points were determined on a MELT.TEMP capillary melting point apparatus at 2°C/min rate of temperature increase and are uncorrected. Infrared spectra were run in KBr discs on a Beckman spectrometer, Model 4260. NMR spectra were recorded on Bruker AM 300 in deuterated acetone, with an internal deuterium lock and both ^1H and ^{13}C chemical shifts are referenced to tetramethylsilane as an internal standard (at δ 0·00). Ultraviolet absorptions were measured in chloroform on a Perkin-Elmer 33 spectrometer.

1-(2-Nitrophenyl-azo)-dihydroxynaphthalenes

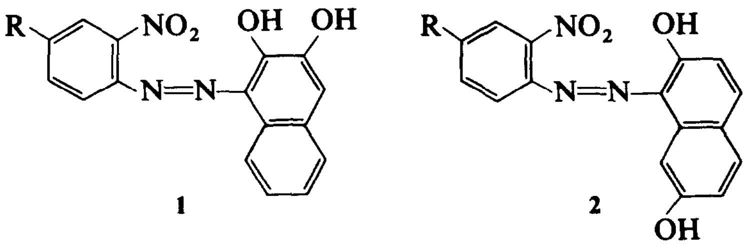
The phenyl azo-dihydroxynaphthalenes were prepared by the usual azo-coupling reactions of the 2,3- and 2,7-dihydroxynaphthalenes with 2-nitrobenzenediazonium chloride and its methoxy and chloro derivatives, using sodium bicarbonate as a coupling reagent. The azo compounds were isolated in nearly quantitative yields.

1-(2-Nitrophenyl-azo)-2-hydroxy-acryloyloxynaphthalenes

The acryloyloxy azo compounds were prepared according to the following general procedure (Scheme 1). To a stirred solution of 1(2-nitrophenyl-azo)-dihydroxynaphthalene (0·009 mol) and sodium hydroxide (0·018 mol) in water (75 cm^3) was added dropwise acryloyl chloride (0·009 mol) in chloroform (40 cm^3). After 2 h stirring at room temperature the organic layer was isolated, dried and evaporated. The resulting product was recrystallized from ethanol.

RESULTS AND DISCUSSION

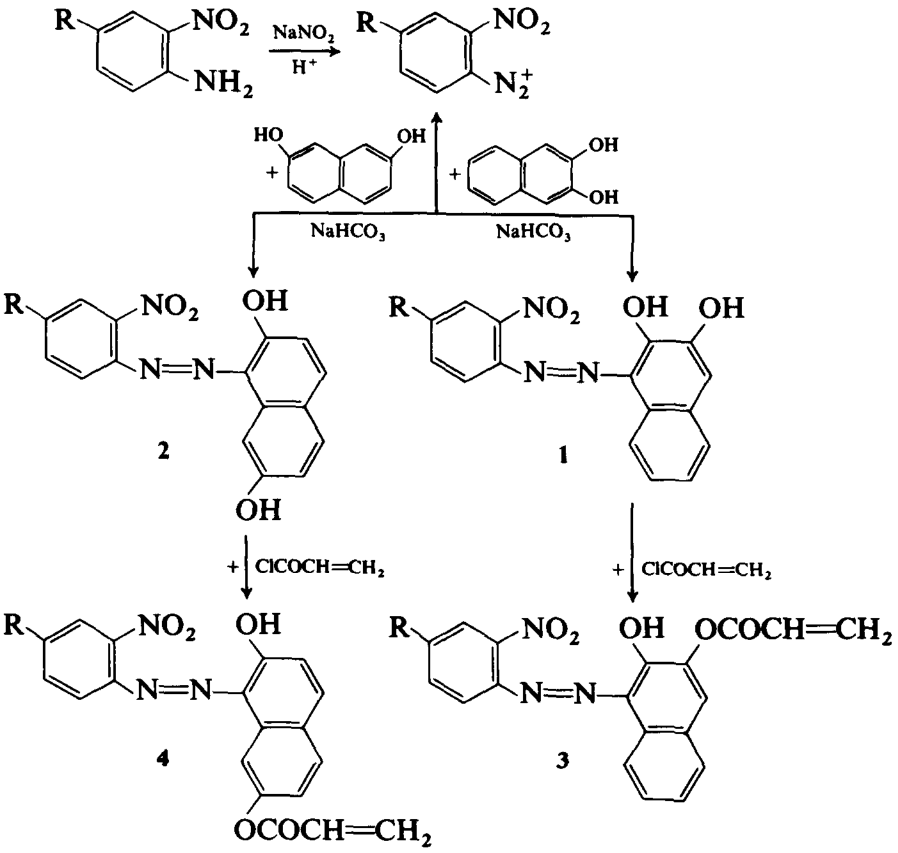
Two series of phenylazo-dihydroxynaphthalenes of the general formulae **1** and **2** were synthesized by azo-coupling reactions of 2-nitrobenzene diazonium salt and its chloro and methoxy derivatives with 2,3- and 2,7-dihydroxynaphthalenes. The coupling reactions involve electrophillic attack by the diazonium salts mainly at the α-position of the 2,3- and 2,7-dihydroxynaphthalenes which resulted in the usual α-substitution products[5] in nearly quantitative yields.



R = H, OCH_3 and Cl

Scheme 1

The esterification of these compounds 1 and 2 with acryloyl chloride was carried out in a phase-transfer reaction of the Schotten–Bauman type. Initially, the acryloyl chloride in chloroform is added to a sodium salt of the phenylazo-dihydroxynaphthalene in an aqueous medium, and, as its reaction with acryloyl chloride proceeds, the product becomes soluble in



R = (a) H, (b) OCH_3 and (c) Cl

Scheme 2

TABLE 1
Properties and Analytical Data for Phenylazo-naphthalenes and their Acryloyloxy Monomers

Pigment	*Substituents R*	*Solvent*	*Appearance*	*m.p.*	*Required (%)*			*Found (%)*		
					C	*H*	*N*	*C*	*H*	*N*
1a	H	DMSO	Dark red	212–214	62·1	3·5	13·6	62·1	3·5	13·5
1b	OCH_3	DMSO	Reddish violet	250–252	60·2	3·8	12·4	60·3	3·9	12·7
1c	Cl	DMSO, H_2O	Reddish brown	210–212	56·0	2·9	12·2	55·6	2·9	12·3
2a	H	DMSO, H_2O	Brown	266–268	62·1	3·5	13·6	61·9	3·6	13·4
2b	OCH_3	DMSO, H_2O	Reddish violet	220–222	60·2	3·8	12·4	60·4	4·0	12·2
2c	Cl	DMSO	Red	242–244	56·0	2·9	12·2	55·8	3·1	12·3
3a	H	EtOH	Red	182–184	62·8	3·6	11·6	62·8	3·6	11·2
3b	OCH_3	EtOH	Red	182–184	61·0	3·8	10·7	60·9	3·7	10·4
3c	Cl	EtOH	Dark red	184–186	57·4	3·0	10·6	57·2	3·0	10·2
4a	H	EtOH	Violet	218–220	62·8	3·6	11·6	62·5	3·4	11·3
4b	OCH_3	EtOH	Red	202–204	61·0	3·8	10·7	60·8	4·0	10·9
4c	Cl	EtOH	Reddish brown	170–172	57·4	3·0	10·6	57·2	3·0	10·4

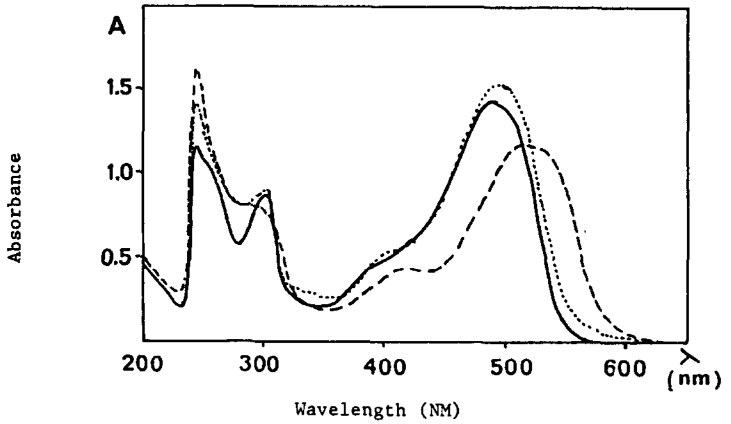


Fig. 1. UV spectra of **3a** (——), **3b** (– – –) and **3c** (.....) in $CHCl_3$, 7×10^{-5} mol dm^{-3}.

chloroform. The organic layer develops color, whereas the aqueous layer becomes colorless. The products were purified by double crystallization from ethanol and were obtained in 41–63% yield. Although two hydroxyl groups are available for the esterification, only the hydroxyl groups in the 3- and 7-positions for compounds **1** and **2** respectively took part in the reaction (Scheme 1). The hydroxyl group in the 2-position remained unreacted, due to an intramolecular hydrogen bond between the OH-group and an azo nitrogen. This was confirmed by ^{1}H NMR, which showed very low field OH-proton signals at 16·3–16·6 ppm, which are typical for protons involved in intramolecular hydrogen bonds.[6] The routes involved in the synthesis are as shown in Scheme 2.

The characterization data for the two series of the phenylazonaphthalenes **1–4(a,b,c)** are summarized in Table 1.

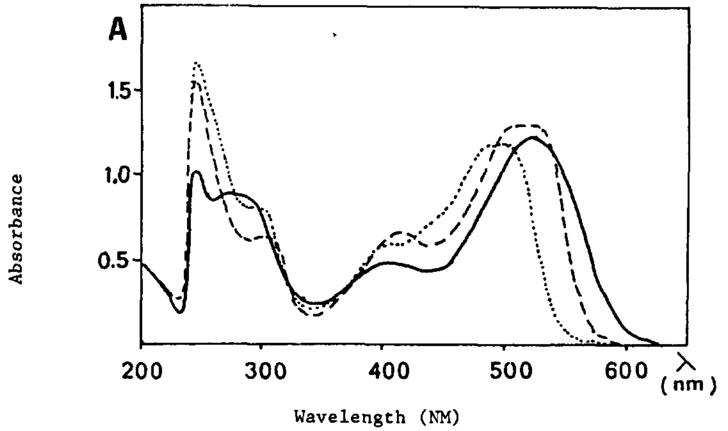


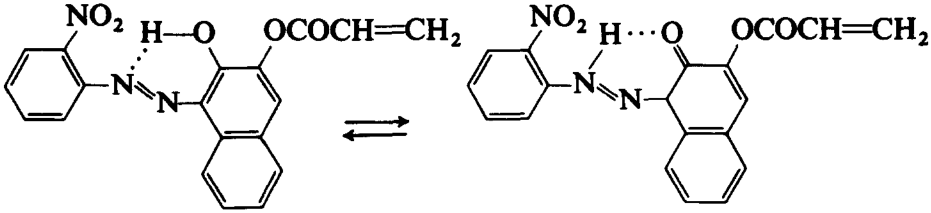
Fig. 2. UV spectra of **4a** (——), **4b** (– – –) and **4c** (.....) in $CHCl_3$, 6×10^{-5} mol dm^{-3}.

The ultraviolet spectral behavior of compounds 3 and 4, was investigated in chloroform and ethanol. Comparing the UV spectra in chloroform (Figs 1 and 2), it was found that all spectra show a strong absorption band in the range of 350 nm to about 600 nm, representing a superposition of at least two individual absorption peaks. According to Haessner *et al.*,[7] these peaks are characteristically for the azo and hydrazone forms. For 1-phenylazo-2-naphthols they obtained the azo-band at about 420 nm and the hydrazone band at about 500 nm. Accordingly, it can be assumed that, in Figs 1 and 2, the shoulder obtained at 390–400 nm represents the azo-form and the peak at 490–520 nm represents the hydrazone-form of the 1(2-nitrophenylazo)-2-hydroxy-3- (and -7-)-acryloyloxynaphthalenes. Comparing the intensity of both absorption bands it can be concluded that, in chloroform the hydrazone form is predominantly present. In ethanol very similar spectra were obtained (Table 2), showing that the effect of solvents on the azo-hydrazone equilibrium is small. These results are in agreement with findings

TABLE 2
UV/Visible Spectra of the Monomeric Acryloyloxy-Azo Compounds **3** and **4**

Compound	*Substituents*	*Chloroform solution*		*Ethanol solution*	
		λ_{max} (*nm*)	$\varepsilon_{max} \times 10^{-4}$ ($dm^3\, mol^{-1}\, cm^{-1}$)	λ_{max} (*nm*)	$\varepsilon_{max} \times 10^{-4}$ ($dm^3\, mol^{-1}\, cm^{-1}$)
3a	H	490·0	2·27	483·5	2·23
		387·0	(S)[a]	385·0	(S)
		303·0	1·39	300·5	1·35
3b	OCH_3	515·5	1·57	509·5	1·41
		420·0	0·59	417·0	0·56
		295·0	1·07	295·0	1·00
3c	Cl	494·0	2·21	486·5	2·11
		404·0	(S)	396·0	(S)
		303·0	1·30	300·0	1·23
4a	H	522·5	2·29	532·5	2·01
		402·5	0·92	352·0	0·78
		282·0	1·67	293·0	1·26
4b	OCH_3	510·0	2·09	505·5	2·04
		415·5	1·08	414·5	1·09
		305·5	1·06	304·0	1·03
4c	Cl	489·0	1·56	485·0	1·43
		400·0	0·77	396·0	(S)
		295·0	1·07	293·5	1·01

[a] S = shoulder.



Scheme 3

of Burawoy *et al.*[8] which showed that 1-nitrophenylazo-2-naphthols exist almost exclusively as phenylhydrazones (Scheme 3).

The ^{1}H NMR spectra for the parent compounds **1** and **2** showed two signals in range of 10·5–11·0 ppm and 16·3–16·6 ppm, attributed to the 2 —OH groups. The lower field signals of —OH groups in the range 16·3–16·6 ppm are typical for protons involved in the azo-hydrazone tautomerism.[6] The introduction of the acrylate group into compounds 1 and 2 resulted in the disappearance of the peaks in the range of 10·5–11 ppm. This confirmed that the esterification occurred at the pendent hydroxyl group at the 3-position in compound **1** and the 7-position in compound **2**.

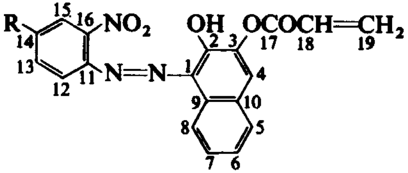
The ^{1}H and ^{13}C NMR spectra of compounds **3** and **4** showed the normal chemical shift values expected for the parent compounds **1** and **2**. In addition, they showed the chemical shifts of the acryloyloxy groups. The ^{1}H NMR spectra for the phenylazo-dihydroxynaphthalenes **1** and **2** and their acryloyloxy monomers **3** and **4** were assigned by the use of ^{1}H homonuclear correlation (COSY) spectra, and were easily assigned by the use of 2D heteronuclear (^{13}C—^{1}H) shift correlation spectroscopy. The ^{1}H and ^{13}C NMR data for compounds **3** and **4** are presented in Tables 3 and 4 and in Tables 5 and 6, respectively. All ^{13}C-chemical shift values listed in Tables 3 and 4 were checked by literature values and the nonprotonated ^{13}C nuclei were assigned on the basis of chemical shifts.[9]

The copolymerization of **3b** and **4b** with styrene was achieved in sealed tubes using chloroethane as solvent. The polymers obtained were subjected to a consequent precipitation procedure to remove the unreacted monomers. The polymers retained their color after five times precipitation, which indicates that the pigment is chemically attached to the polymer chain. Copolymerization of the azo-naphthol monomer **3b** with styrene (1% 3b/St) gave copolymers with a weight average molecular weight ($\bar{M}_w$) of 36 700 g mol^{-1}. The number average molecular weight ($\bar{M}_n$) was 4100 g mol^{-1}. In the copolymerization of **4b** with styrene, the weight average molecular weight ($\bar{M}_w$) of 27 100 g mol^{-1} and the number average molecular weight ($\bar{M}_n$) was 8400 g mol^{-1}.

The copolymers obtained show strong absorption bands in the range of 350–600 nm, in agreement with the behavior of the azo naphthol monomers.

TABLE 3

^{1}H NMR Chemical Shift Data for Phenylazo-acryloyloxynaphthalene Compounds **3a**, **3b** and **3c**

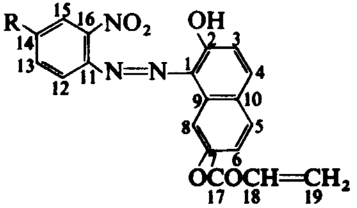


Group assignment	*Chemical assignment*	Chemical shift in ppm		
		3a	**3b**	**3c**
Naphthyl group	4	6·95 (1H, S)	7·25 (1H, S)	6·65 (1H, S)
	5, 6, 7,	7·40 (4H, m)	7·40 (5H, m)	7·4 (4H, m)
	2	16·4 (1H, S, —OH)	16·35 (1H, S, —OH)	16·4 (1H, S, —OH)
Phenyl azo group	14	7·25 (1H, ddd, J 8·8, 8·9 and 1·0 Hz)	— — —	— — —
	13	7·75 (1H, ddd, J 8·8, 9·0 and 1·0 Hz)	[a]	7·8 (1H, dd, J 9·1 and 2·3 Hz)
	15	8·30 (1H, d, J 8·9 Hz)	7·7 (1H, d, J 2·4 Hz)	8·20 (1H, d, J 2·3 Hz)
	12	8·35 (1H, d, J 9·0 Hz)	8·35 (1H, d, J 8·7 Hz)	8·30 (1H, d, J 8·7 Hz)
	—OMe	— — —	3·96 (3H, S, OCH_3)	— — —
Acryloyloxy group	18	6·42 (1H, dd, J 10·2 and 17·4 Hz)	6·42 (1H, dd, J 10·4 and 17·3 Hz)	6·40 (1H, dd, J 10·4 and 17·5 Hz)
	19 *cis*	6·10 (1H, dd, J 10·2 and 1·15 Hz)	6·10 (1H, dd, J 10·4 and 1·1 Hz)	6·15 (1H, dd, J 10·4 and 1·1 Hz)
	19 *trans*	6·65 (1H, dd, J 17·4 and 1·15 Hz)	6·65 (1H, dd, J 17·3 and 1·1 Hz)	6·65 (1H, dd, J 17·5 and 1·1 Hz)

[a] Overlapping with protons 5, 6 and 7.

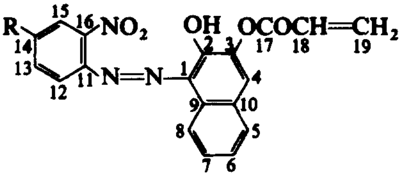
TABLE 4

^{1}H NMR Chemical Shift Data for Phenylazo-Acryloyloxy Compounds **4a**, **4b** and **4c**



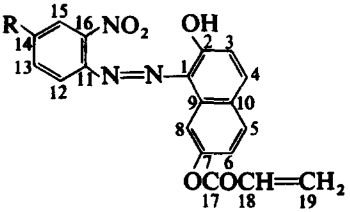
Group assignment	Chemical assignment	Chemical shift in ppm		
		4a	**4b**	**4c**
Naphthyl group	3	6·5 (1H, d, J 9·5 Hz)	6·60 (1H, d, J 9·5 Hz)	6·40 (1H, d, J 9·5 Hz)
	6	7·0 (1H, dd, J 8·4 and 1·7 Hz)	7·10 (1H, dd, J 8·3 and 1·7 Hz)	7·0 (1H, dd, J 8·5 and 1·7 Hz)
	5	7·6 (1H, d, J 8·4 Hz)	7·60 (1H, d, J 8·3 Hz)	7·5 (1H, d, J 8·5 Hz)
	4	7·8 (1H, d, J 9·5 Hz)	7·80 (1H, d, J 9·5 Hz)	7·75 (1H, d, J 9·5 Hz)
	8	7·85 (1H, d, J 1·7 Hz)	7·85 (1H, d, J 1·7 Hz)	7·80 (1H, d, J 1·7 Hz)
	2	16·6 (1H, S, —OH)	16·5 (1H, S, —OH)	16·6 (1H, S, —OH)
Phenyl azo group	14	7·25 (1H, ddd, J 8·6, 8·8 and 1·0 Hz)	— — —	— — —
	13	8·0 (1H, ddd, J 8·6, 8·8 and 1·0 Hz)	7·6 (1H, dd, J 9·3 and 1·3 Hz)	7·95 (1H, dd, J 9·3 and 1·3 Hz)
	15	8·35 (1H, d, J 8·8 Hz)	7·75 (1H, d, J 1·3 Hz)	8·25 (1H, d, J 1·3 Hz)
	12	8·45 (1H, d, J 8·60 Hz)	8·45 (1H, d, J 9·3 Hz)	8·45 (1H, d, J 9·3 Hz)
	OMe	—	4·0 (3H, S)	—
Acryloyloxy group	18	6·35 (1H, dd, J 10·5 and 17·3 Hz)	6·35 (1H, dd, J 10·5 and 17·3 Hz)	6·40 (1H, dd, J 10·5 and 17·3 Hz)
	19 *cis*	6·10 (1H, dd, J 10·5 and 1·1 Hz)	6·10 (1H, dd, J 10·5 and 1·1 Hz)	6·15 (1H, dd, J 10·5 and 1·2 Hz)
	19 *trans*	6·65 (1H, dd, J 17·3 and 1·1 Hz)	6·65 (1H, dd, J 17·3 and 1·1 Hz)	6·65 (1H, dd, J 17·3 and 1·2 Hz)

TABLE 5
^{13}C NMR Data for Phenylazo-Acryloyloxy Compounds **3a**, **3b** and **3c**



	Chemical shift (ppm)									
Naphthyl group	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10
3a	135·8	175·0	148·0	118·5	128·0	123·5	127·0	129·0	129·5	131·0
3b	135·0	173·0	148·5	119·5	127·8	124·5	127·3	129·0	129·2	131·5
3c	135·5	174·5	148·5	119·0	128·2	123·8	127·0	129·3	129·5	131·5
Phenyl azo group	C-11	C-12	C-13	C-14	C-15	C-16	OMe			
3a	139·0	118·0	125·0	136·0	126·5	144·0				
3b	137·5	122·5	132·0	156·5	108·0	144·0	56·0			
3c	138·0	123·0	134·0	136·0	126·0	144·5				
Acryloyloxy group	C-17	C-18	C-19							
3a	164·0	127·8	133·5							
3b	164·0	127·8	133·5							
3c	164·0	128·0	133·5							

TABLE 6
^{13}C NMR Data for Phenylazo-Acryloyloxy Compounds **4a**, **4b** and **4c**



	Chemical shift (ppm)									
Napthyl group	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10
4a	135·8	177·5	123·2	132·2	132·0	117·0	161·0	109·0	122·8	133·0
4b	136·0	177·5	123·6	132·5	132·0	117·5	161·0	109·0	123·0	132·0
4c	136·0	182·0	123·8	133·0	132·5	117·5	161·0	110·0	122·8	130·0
Phenyl azo group	C-11	C-12	C-13	C-14	C-15	C-16	OMe			
4a	139·0	118·0	124·8	136·5	126·5	144·8				
4b	138·0	120·0	132·5	157·5	108·0	144·0	56·0			
4c	139·0	120·0	136·8	133·5	126·0	145·2				
Acryloyloxy group	C-17	C-18	C-19							
4a	165·0	128·0	133·5							
4b	165·2	128·0	133·0							
4c	165·0	128·0	133·2							

The band at 400–420 nm represents the azo-form, while the band at 480–515 nm represents the hydrazone form of the phenylazo–naphthalene system. From the high intensity of the latter it can be assumed, that the polymers predominantly exist in the hydrazone-form, as do the monomers.

REFERENCES

1. Konstantinova, N. T., *Dyes and Pigments*, **10** (1988) 63.
2. Hua, Z. Z., Chang, C. K., Xiong, L. J., Ling, C. S. & Lan, W. S., *Dyes and Pigments*, **11** (1989) 277.
3. Alberghina, G., Amato, M. E. & Fisichella, S., *Dyes and Pigments*, **7** (1986) 33.
4. Liqi, H., Zhenghua, Z., Kongchang, C. & Faxiang, Z., *Dyes and Pigments*, **10** (1989) 195.
5. Freeman, S. H., Whaley, W. M., Esancy, M. E. & Esancy, J. F., *Dyes and Pigments*, **7** (1986) 215.
6. Berrie, H. A., Hampson, P., Longworth, S. W. & Mathia, A., *J. Chem. Soc. (B)* (1968) 1308.
7. Haessner, R., Mustroph, H. & Bordsdorf, R., *Dyes and Pigments*, **6** (1985) 277.
8. Burawoy, A., Salem, A. G. & Thompson, A. R., *J. Chem. Soc.* (1952) 4793.
9. Yoshida, S., Lillya, P. C. & Vogl, O., *J. Polym. Sci., Chem. Ed.*, **20** (1982) 2215.