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Polymeric azo pigments

2. Synthesis and characterization of azo naphthol containing polymers

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Summary

1-(2-Nitrophenylazo)-2-hydroxy-acryloyloxynaphthalenes were polymerized and copolymerized with styrene in dichloroethane using AIBN as the initiator. The resulting colored polymers were characterized by U.V. spectroscopy and their molar masses were determined using Size Exclusion Chromatography. It was shown that the obtained products consist of mixtures of the appropriate copolymers and homopolymerized acryloyl-azo naphthols.

Introduction

The formation of colored coatings usually involves the imbedment of a monomeric pigment into a polymeric matrix. Classically this is done by mixing both components, thus leaving the pigment chemically independent in the final coating matrix. The pigment may then migrate out of the surface resulting in quality losses of the coating. Recently extensive work has been undertaken to introduce dyes (1) and pigments (2-4) into the backbone of the polymer chain to form colored compositions resistant to solvents and having high durability. In order to prepare polymerizable pigments, which can be chemically bound to a polymer backbone, we esterified 1-(2-nitrophenylazo)-dihydroxynaphthalenes with acryloyl chloride and obtained the appropriate acryloyloxy compounds (5).

In the present work we wish to report the polymerization and copolymerization behaviour of the azo naphthol monomers using styrene as the comonomer. It was the objective to determine the chemical composition and the molar mass distribution of the resulting polymers.

Experimental

The synthesis of the 1-(2-Nitrophenylazo)-2-hydroxy-acryloyloxynaphthalenes was described in a previous paper (5). Styrene was distilled twice immediately before use. All solvents were analytical or spectroscopical grade. AIBN was recrystallized from dry methanol. The absorption spectra were recorded on a SHIMADZU spectrophotometer UV-160 using chloroform as solvent.

The SEC measurements were carried out on a WATERS High Performance Gel Permeation Chromatograph LC 244, equipped with R.I. and U.V. (313 nm) detectors. A column system consisting of ULTRASTYRAGEL 500 A and linear, 30 cm x 7.8 mm I.D., was used. The flow rate was 1 ml/min, 50 µl of 1% polymer solutions in THF were injected using a WISP Model 710 B sample processor (WATERS). Data processing was carried out on a WATERS Model 730 data model with GPC option.

Homopolymerizations were achieved in chloroethane solution using AIBN in glass tube. The homogenious mixture was degassed by three freeze-thaw cycles. The tube was sealed

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Table 1. Summary of the Polymerization Experiments

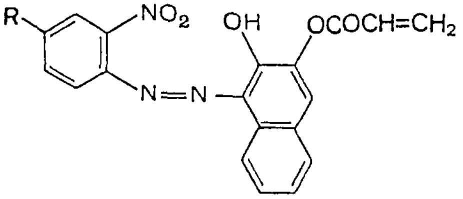
Sample	Comonomer Azo Monomer (g)	Amount Styrene (g)	Polymerization time (hours)	Color	Yield (wt. %)
I	0.034	0.966	120	orange	39
II	0.037	0.963	120	violet	36
III	0.034	0.966	120	red	28
IV	0.037	0.963	120	pink	31

at 0.02 mm Hg and placed in a constant temperature bath at 60°C. After 5 days the tube was opened and the solution was added dropwise with stirring to ethanol (200 ml). The suspension was allowed to settle for 1 h and filtered. The solid polymer was dissolved in chloroethane and precipitated again from ethanol, collected by filtration, washed with ethanol (60 ml) and dried under reduced pressure for 2 days.

Procedures for the copolymerization with styrene (St) were similar to the homopolymerization process. The amounts of materials used for the polymerization and the yields are presented in Table 1.

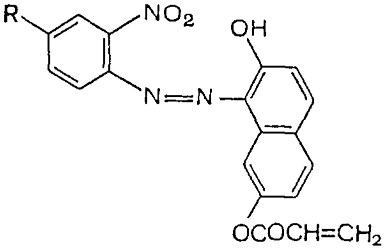
Results and Discussion

The following monomers were used in this study:



I : R = H

II : R = OCH_3



III : R = H

IV : R = OCH_3

Polymerizations of I – IV were achieved in sealed tubes using chloroethane as solvent and AIBN as initiator. A consequent reprecipitation procedure was aimed at removing unreacted monomers. It was found that 1% concentration of the pigment in the initial monomer mixture was sufficient to obtain colored polymers. These polymers retained their color after 5 times precipitation to remove the unreacted pigment, which indicates that the pigment is chemically bound to the polymer chain.

The molar mass and the polydispersity of the products were determined by SEC using ultrastyragel as stationary phase and tetrahydrofurane as eluent. A calibration curve was built from polystyrene samples of narrow molecular weight distribution (4.10^3 - 3.10^6).

During the separation both the refractive index and the U.V. signal were recorded and the molar mass as well as the polydispersity were calculated from the refractive index signal.

The U.V. spectroscopical behaviour of the polymers was investigated in chloroform. The U.V. spectra are presented in Figure 1 and the appropriate data are summarized in Table 2.

Table 2. U.V. Spectroscopical Data of the Azo Naphthol Containing Polymers

Compound	λmax (mm)	lg ε
Poly - I	489.0 400.0 304.0	4.313 shoulder 4.123
1% I/St	483.0 294.0	
Poly - II	515.0 418.0 300.0	4.350 3.989 4.055
1% II/St	513.5 411.0 300.0	
1% III/St	482.0 384.5	
Poly - IV	506.0 418.0 300.0	4.122 3.849 3.865
1% IV/St	502.0 415.5 374.0	

In agreement with the behaviour of the azo naphthol monomers (5) the polymers show strong absorption bands in the range of 350 to 600 nm where the band at 400-420 nm represents the azo-form. Accordingly 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, similar to the monomers, predominantly exist in the hydrazone-form.

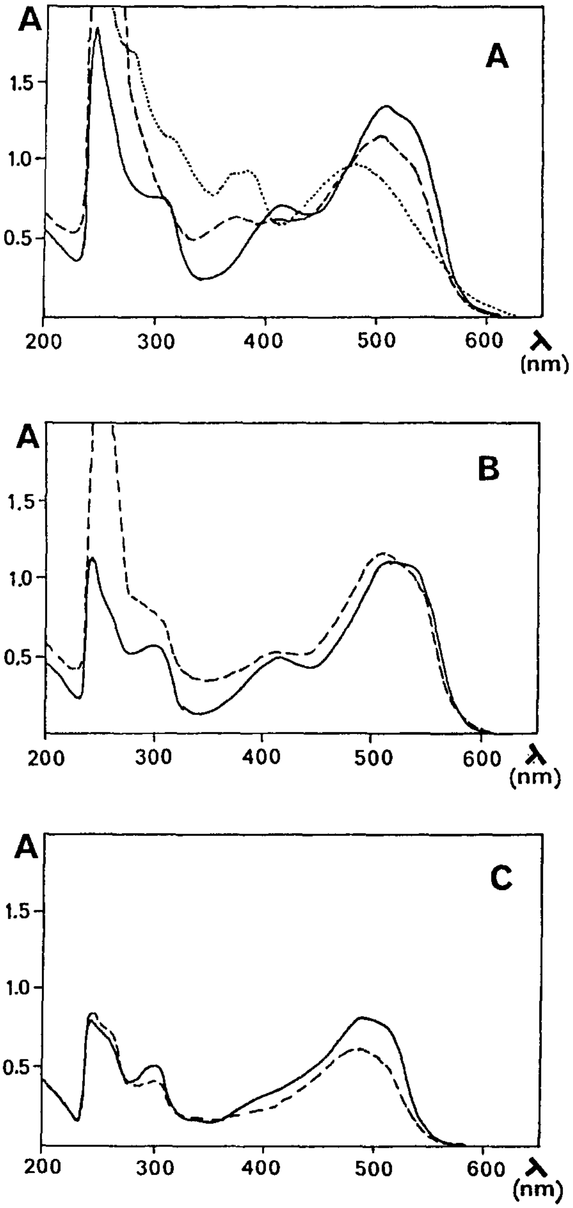
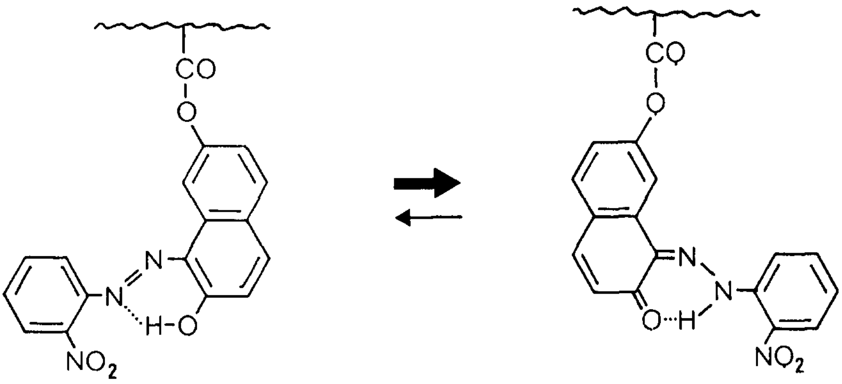


Figure 1. UV spectra of the homopolymers (______) and copolymers (----) in $CHCl_3$; IV (A), II (B), I (C), CO – III/St (....).



For the copolymers the amounts of incorporated azo naphthol units were calculated from the extinction coefficients of the appropriate homopolymers (I, II) and monomers (III, IV). They are:

Copolymer System	Amount of Azo Naphthol	
	Monomer Mixture	Copolymer
I/St	1 Mol. %	3.1 Mol. %
II/St	1 Mol. %	1.9 Mol. %
III/St	1 Mol. %	1.8 Mol. %
IV/St	1 Mol. %	1.3 Mol. %

In order to obtain information about the molar mass distribution of the polymers, they were subjected to Size Exclusion Chromatography with simultaneous refractive index and ultraviolet detection. The SEC chromatograms are presented in Figures 2 and 3.

In all cases the U.V. profiles were found to be similar to the R.I. profiles, indicating the azo naphthol units are uniformly distributed over the different molar mass fractions. Poly - I gave a normal distributed SEC profile (see Figure 2); a small peak in the monomer region of the UV profile showed, that a small amount of unreacted monomer was present in the product. In the case of a copolymer of I with styrene two peaks were obtained both in the R.I. and U.V. profile. From its elution volume the peak in the low molar mass region can be assigned to unreacted azo naphthol monomers whereas the other peak belongs to a co-oligomer with an average molar mass of about 800. Different from I the azo naphthol II

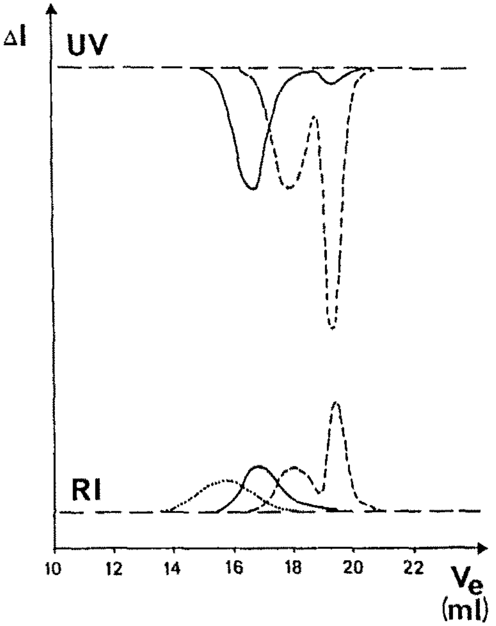


Figure 2. SEC chromatograms of azo naphthol polymers; Poly - I (____), 1% I/St (----), 1% II/St (...).

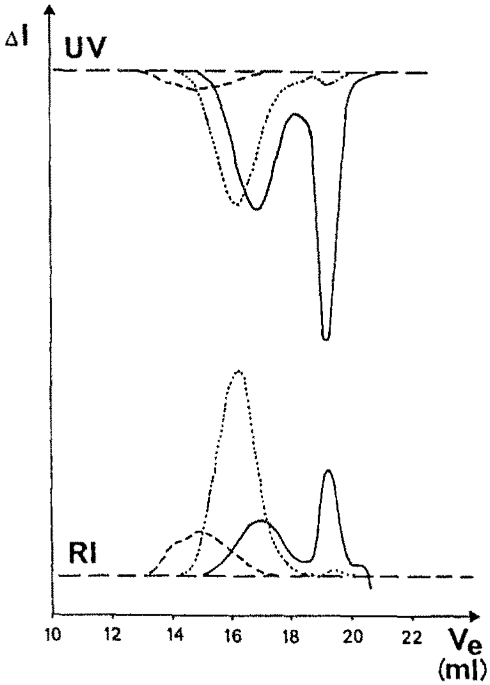


Figure 3. SEC chromatograms of azo naphthol polymers; 1% III/St (...), Poly - IV (____), 1% IV/St (---).

showed a better copolymerization behaviour resulting in a copolymer without residual azo naphthol monomer. As for the copolymerization of III and IV with styrene, also the appropriate copolymers were obtained containing only minor amounts of unreacted azo naphthol monomer (1% III/St). As could be expected, the homopolymerization resulted in a mixture of the homopolymer (molar mass ~ 2000) and unreacted monomer.

The molar masses of the normally distributed products are summarized in Table 3.

Table 3. Molar Masses of Polymers Obtained by SEC

Sample	$\bar{M}n$	$\bar{M}w$	$\bar{M}w/\bar{M}n$
Poly - I	1.700	7.700	4.5
1% II/St	4.100	36.700	8.9
1% III/St	2.900	12.300	4.3
1% IV/St	8.400	27.100	3.2

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3. Bonnet, E. J. (1983) U.S. Pat. 4,381,261.
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