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Reactive Polymeric Dyes as Textile Auxiliaries

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Summary: Commercial and synthetic azobenzene derivatives were used for the synthesis of hydrophilic polymeric dyes. Two strategies based respectively on the polymerization of dye methacrylic derivatives with different monomers and on the functionalization of reactive polymers were investigated. Polymers containing rather small amounts of the selected dyes were generally obtained, very likely because of the electron withdrawing effect of azo chromophores. Almost quantitative conversions were recorded in the reaction of commercial dyes with maleic anhydride/methyl vinyl ether alternating copolymers. Some of the prepared polymeric dyes were preliminarily tested as textile finishing agents.

Keywords: azo polymers; functionalization of polymers; hydrophilic polymers; polymeric dyes; textile auxiliaries

Introduction

Several polymeric materials have found application in the textile industry for size stabilization of fabrics made of natural fibers and for modifying their water and oil repellence.[1] Much research is being devoted as well to the development of more environmentally friendly dyeing agents and processes.[2] In this respect, polymeric dyes are very attractive because of their macromolecular nature that inhibits dye migration. Additionally, they can form stable bonds with fibers,[3] and modify the tactile response and the hydrophilic-hydrophobic balance of textiles, whereas the use of suitable comonomers allows for easy modulation of their properties. Azobenzene containing polyacrylates and polymethacrylates,[4-6] dye-terminated oligo(ester)s and oligo(amide)s,[7,8] polycondensation products of diacids with difunctional monomeric dyes,[9] and polymeric dyes produced by reaction of preformed reactive polymers with conventional dyeing products.[9-11] were investigated as candidate dyes.

Following our interest in azobenzene polymers,[12-15] in the present paper we report some of the results obtained in the research on functional polymeric dyes, potentially useful as textile

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auxiliaries. The prepared materials could find application also in other market segments, for the production of cosmetics, dye-laser dyes, and inks. Attention was focused on azobenzene polymers containing hydrophilic monomeric units and/or reactive groups that might improve both color-fastness and size stability of dyed fibers. These materials were obtained by polymerization of monomeric dyes with different comonomers and by chemical modification of preformed reactive polymers. Some very preliminary dyeing tests were also performed.

Experimental Part

Monomers and reagents

6-Amino-2-(4-carboxyphenylazo)-1-hydroxynaphthalen-3-sulfonic acid (ACNS), 6-amino-2-phenylazo-1-hydroxynaphthalen-3-sulfonic acid (AFNS), 1-(3-methyl-4-(3-methylphenyl-azo)phenylazo)naphthyl-2 methacrylate (SRBMA), and 4-methacrylamido-2',3-dimethylazo-benzene (FGMAm) were prepared as already reported.[13,14]

Polymerization experiments

A 5-10% monomer solution and the planned amount of AIBN in anhydrous benzene was placed in a vial. After 3 freeze-pump-thaw cycles, the vial was sealed under vacuum and heated at 60 °C for 36 h. The reaction mixture was poured in excess non-solvent, the coagulated product was reprecipitated and dried under vacuum up to constant weight.

Functionalization of preformed polymers

Experiments were carried out according to the following procedure: dye, reactive polymer, and solvent were heated at the designed temperature for 72 h. After cooling at room temperature, the reaction product was coagulated in a non-solvent and dried under vacuum to constant weight. The extent of functionalization was evaluated by ^{1}H-NMR and/ FT-IR spectroscopy.

Application of polymeric dyes to fabric samples

Dyeing tests were performed by suspending three squares (5x5 or 10x10 cm) of white cotton, combed wool, or raw wool in 50-150 ml of dye solution in either water (pH 7.8) or ethanol at

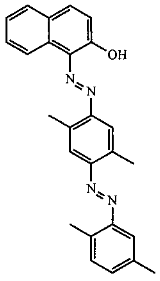
60 °C for 1 h under gentle stirring. The wet fabric samples were wrung, and left to dry in air. Both the starting and the spent dyeing solutions were analyzed by UV spectroscopy.

Product characterization

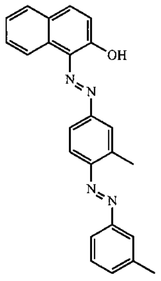
FT-IR spectra were recorded on cast films with mod. 1640 Perkin-Elmer spectrophotometer. ^{1}H NMR spectra were recorded at 200 MHz on 5-10 % sample solutions in perdeuterated solvents with a Varian Gemini 200 spectrometer,. UV-vis spectra were recorded between 250 and 700 nm at 25 °C in 1 cm quartz cells with Jasco Uvidec 510 spectrophotometer. Size exclusion chromatography (SEC) analyses were carried out in chloroform with a 600E Waters liquid chromatograph equipped with two PL Mixed C 5 μm columns, 486 Waters UV detector, and 410 Waters RI detector, by using polystyrene standards for calibration. SEC analyses of water-soluble polymers were carried out by using two Ultrahydrogel Linear columns, by using 0.1M $LiNO_3$ as eluent and poly(vinyl alcohol) standards for calibration.

Results and Discussion

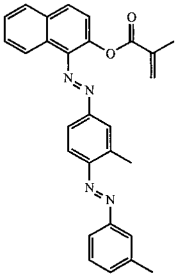
Commercial monofunctional dyes, i.e. 2-hydroxy-1-(3-methyl-4-(3-methylphenylazo)phenylazo)naphthalene (Sudan Red B, SRB), 2-hydroxy-1-(2,5-dimethyl-4-(2,5-dimethylphenylazo)phenylazo)naphthalene (Oil Red O, ORO), and 4-amino-2',3-dimethylazobenzene (Fast Garnet GBC base, FG) were used for the preparation of functional polymeric dyes.



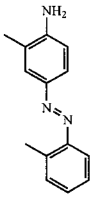
ORO



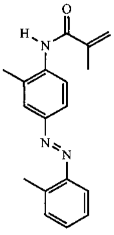
SRB



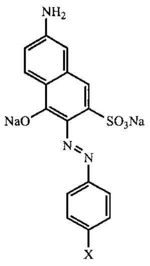
SRBMA



FG



FGMAm



AFNS (X = H)
ACNS (X = COOH)

Dyes containing both one reactive amino group and hydrophilic ionizable groups, 6-amino-2-(4-carboxyphenylazo)-1-hydroxynaphthalen-3-sulfonic acid (ACNS) and 6-amino-2-phenylazo-1-hydroxynaphthalen-3-sulfonic acid (AFNS) were prepared in 75 and 77% yield, respectively.[13] Reaction of SRB and FG with methacryloyl chloride afforded two polymerizable dyes, i.e. SRBMA and FGMAm in 80 and 57% yield, respectively.[13.14]

Preparation of polymeric dyes by polymerization

Free radical homopolymerization of SRBMA was investigated in benzene solution in the presence of 1-6% of either 2,2'-azobis*iso*butyrronitrile (AIBN) or benzoylperoxide (BPO). Independent of initiator type and amount, no polymeric product was formed and the monomer was recovered almost quantitatively (Table 1). These results demonstrated that SRBMA does not undergo radical homopolymerization and that the monomer is not involved in secondary reactions. No polymeric product was formed when the polymerization was performed by using 25% /BPO. ^{1}H-NMR analysis of the reaction mixture suggested that the phenyl radical formed by BPO decomposition added to the polymerizable double bond. Very likely, this radical cannot propagate the polymerization chain due to electronic effects.

Copolymerization of 5:95 SRBMA/methyl methacrylate (MMA) mixture with 2 % BPO gave 35 % yield of product containing 7 % SRBMA units, indicating the larger reactivity of the SRBMA. The average number molecular weight (4 kDa) of this product is one order of magnitude lower than that of poly(MMA) prepared under the same conditions. Moreover, SEC analysis indicated that SRBMA acted as chain-transfer and/or chain-terminating agent. No polymer was formed when SRBMA was copolymerized with N-vinyl-2-pyrrolidinone (NVP). Indeed, SRBMA double bonds should be more electron-poor than MMA, suggesting a strong tendency to alternate polymerization. In this case, the reaction of NVP with a free radical should be followed by addition of SRBMA, which is unable to add further units.

Copolymerization of SRBMA with MAA, by varying solvent, feed composition, type, and amount of initiator afforded only rather low conversions to polymers containing less dye units than the corresponding feed. Comparison of SEC traces recorded by using RI and UV detectors suggests that the copolymerization products are constituted by MAA polymer chains terminated by one SRBMA unit.

Table 1. Copolymerization of polymerizable azo dyes (M_1) with different monomers (M_2).[a]

M_1	M_2		Initiator		Temp.[b]	Duration	Yield	M_2 polymer	M_n
	type	% mol	type	%	°C	h	%	% mol	kDa
FGMAm	–	–	AIBN	1	60	36	72	–	27
SRBMA	–	–	AIBN	4	65	72	0	–	–
SRBMA	–	–	AIBN	6	65	72	0	–	–
SRBMA	–	–	BPO	2	70	72	0	–	–
SRBMA	–	–	BPO	25	70	72	0	–	–
FGMAm	NVP	10	AIBN	1	70	48	53	6	7
FGMAm	NVP	50	AIBN	1	70	48	21	32	6
FGMAm	NVP	90	AIBN	1	60	36	4	46	5
FGMAm	NVP[c]	90	AIBN	1	65	48	11	65[d]	6
FGMAm	NVP	95	AIBN	1	65	48	4	60	5
SRBMA	NVP	95	AIBN	1	65	65	0	–	–
SRBMA	NVP	95	BPO	2	65	65	0	–	–
–	NVP	100	AIBN	1	65	65	99	100	49
FGMAm	MMA	90	AIBN	1	65	48	92	89	23
FGMAm	MMA[c]	90	AIBN	1	60	36	94	90[e]	28
SRBMA	MMA	95	BPO	1	65	65	35	93	4
–	MMA	100	BPO	1	65	65	78	100	25
FGMAm[f]	MAA	80	AIBN	2	70	48	73	79	7
FGMAm[f]	MAA	90	AIBN	2	70	48	94	92	7
SRBMA[f]	MAA	90	AIBN	1	65	65	21	98	9
SRBMA[f]	MAA	90	BPO	2	65	65	1	98	7
FGMAm	NTBAm	85	AIBN	1	65	80	93	84	27
FGMAm	NTBAm	90	AIBN	1	65	80	97	89	26
FGMAm	NTBAm	95	AIBN	1	65	80	97	94	29
–	NTBAm	100	AIBN	1	65	80	78	100	49
FGMAm	VAc	85	AIBN	1	60[g]	52	19	49	4
FGMAm	VAc	90	AIBN	1	60[g]	52	14	50	3
FGMAm	VAc	95	AIBN	1	60[g]	52	9	53	2
–	VAc	100	AIBN	1	60[g]	52	75	100	12

[a] In benzene if not otherwise stated

[b] Heating was continued for further 2 hours at 90 °C when BPO was used as initiator.

[c] The polymerization feed contained 5% of GMA.

[d] The polymerization product contained 10% of GMA units.

[e] The polymerization product contained 5% of GMA units.

[f] Run carried out in dioxane.

[g] After 48 h the temperature was raised at 70 °C.

Homopolymerization of FGMAm in benzene solution at 60 °C in the presence of 1% AIBN afforded 72% yield of orange polymer with M_n = 27 kDa and polydispersity index of 2.8. Copolymerization of 9:1 MMA/FGMAm mixture in benzene at 65 °C in presence of 1%

AIBN gave 92% yield of orange polymer having similar composition to the polymerization feed. SEC analysis highlighted monomodal molecular weight distribution with M_n = 24 kDa and M_w/M_n = 1.9. The identity of curves recorded with RI and UV detectors is in agreement with a random distribution of structural units derived from the two monomers.

Terpolymerization of 10:85:5 FGMAm/MMA/glycidyl methacrylate (GMA) in benzene afforded 94% of orange polymer having the same composition as the polymerization feed. SEC analysis of the polymeric product indicated monomodal molecular weight distribution with M_n = 28 kDa and M_w/M_n = 3.1. The correspondence of RI and UV curves is again in agreement with a random distribution of monomeric units.

In the copolymerization of FGMAm and NVP, the polymer yield increased from 4 to 53% on increasing the FGMAm feed from 5 to 90%. Under the same conditions, NVP homopolymerization afforded 99% yield. Both molecular weight and polydispersity slightly increased with the FGMAm content These results confirm the difficulty of forming methacrylic copolymers of azo dyes with NVP.[16] NMR analysis indicated that copolymers prepared with excess NVP are constituted by equimolar amounts of comonomers, whereas the NVP content substantially decreases in the products from FGMAm-rich feeds. The reactivity ratios (r_{FGMAm} = 1.97, r_{NVP} = 0.09) evaluated by the Kelen and Tüdös method suggested the formation of macromolecules, in which NVP units are included between either FGMAm units or short sequences, depending on the polymerization feed composition. This behavior was attributed to the electron-rich and electron-poor nature of NVP and FGMAm, respectively.

In order of disposing of water-dispersible polymeric dyes that are able to form covalent bonds with fabric fibers, polymerization of 85:10:5 NVP/FGMAm/GMA mixture was performed in benzene at 65 °C in the presence of 1% AIBN. NMR analysis of the polymeric product, obtained in 11% yield, showed a 55:35:10 NVP/FGMAm/GMA molar ratio. It is worth noting that the molar content of FGMAm and GMA units is almost equal to that of NVP, in agreement with the tendency to alternation of methacrylic monomers and NVP.

Copolymerization of FGMAm/methacrylic acid (MAA) mixtures containing 10 and 20% FGMAm was performed in dioxane at 70 °C in the presence of AIBN. Polymeric products soluble in basic water and having almost the same composition of the feed were obtained in 73 and 94% yield, respectively. SEC analysis of copolymer sodium salts (0.1 M $LiNO_3$ eluent) indicated that both samples are characterized by medium-low molecular weights and by rather large polydispersity indexes, very likely attributable to their polyanion nature.

Copolymerization of FGMAm with vinyl acetate (VAc) was investigated in either benzene or THF solution, by varying the FGMAm feed content between 5 and 15%. In both solvents rather low yields (5-19%) were obtained, whose extent increased as the VAc feed decreased. Copolymer M_n increased on decreasing VAc content, but never exceed ed3.5 kDa. In all cases, the FGMAm content was close to 50%, indicating a strong tendency to alternate polymerization ($r_{FGMAm} = 0.49$ and $r_{VAc} = 0.01$ in benzene, $r_{FGMAm} = 0.71$ and $r_{VAc} = 0.01$ in THF).

Copolymerization of FGMAm with 85-95% N-*ter*butylacrylamide (NTBAm), in benzene at 65 °C in the presence of 1% AIBN, afforded in all cases more than 90% polymeric products having almost the same composition as the feed. The polymer molecular weights were almost independent of polymer composition, whereas M_w/M_n increased from 3.9 to 7.6 with the increasing NTBAm content. However, SEC plots recorded with RI or UV detectors are monomodal and almost identical, ruling out the formation of complex polymer mixtures.

Polymeric dyes by functionalization of preformed reactive polymer

Functionalization of MMA/GMA copolymers containing 10-90% GMA units with SRB, either in benzene in the presence of triethylamine or in dioxane by using NaOH as base gave 0.1 and 8% conversion of the glycidyl groups (Table 2). Very low azo dye contents (0.1-0.9%) were reached also by reacting the same copolymers with AFNS, ACNS, and FG. On the other hand, dark-violet crosslinked polymers were obtained by reaction of SRB in dioxane by using sodium as base or in bulk at 185 °C. Bright-red insoluble products were also formed by reaction of FG with polymer samples containing 30 or 100% GMA units, possibly because base-catalyzed polymerization of side-chain epoxy groups. A soluble yellow solid containing about 7% of FG was obtained by using a polymer containing 13 % of GMA and 10:1 dye/epoxide molar ratio. However, spontaneous crosslinking occurred in a few days.

Table 2. Functionalization of reactive polymers with different dyes.

Dye		Reactive group		Solvent	Catalyst		Temp.	Duration	Conv.[a]
type	mmol	type	mmol	type	type	mmol	°C	h	%
SRB	0.66	GMA	0.62	benzene	NEt$_3$	0.72	80	48	0.1
SRB	0.33	GMA	0.30	dioxane	NaOH	0.25	105	72	8
SRB	2.80	GMA	2.02	dioxane	NaOH	2.02	105	72	–
SRB	0.26	GMA	0.14	none	none	–	185	24	–
AFNS	0.27	GMA	0.62	DMSO	none	–	85	40	0.4
AFNS	1.70	GMA	0.11	dioxane	none	–	105	72	0.5
FG	1.64	GMA	3.73	none	none	–	110	72	nd
FG	0.72	GMA	0.48	benzene	none	–	80	48	3
FG	1.69	GMA	1.13	dioxane	none	–	105	72	3
FG	8.40	GMA	0.93	none	none	–	110	72	nd
FG	1.04	GMA	0.10	none	none	–	110	72	50
SRB	5.00	MAA	5.00	DMF	DMAP[b]	5.0	25	72	5
FG	5.02	MAA	5.00	DMF/dioxane	DMAP[b]	5.0	25	85	0.1
FG	3.64	MAA	5.00	DMF/dioxane	DMAP[b]	5.0	25[c]	100	0.1
SRB	6.4	AnM	6.4	dioxane	none	–	105	48	> 95
SRB	6.4	AnM	6.4	dioxane	TSOH	0.13	105	48	> 95
SRB	6.4	AnM	6.4	dioxane	NEt$_3$	6.40	105	48	> 95
PMF	12.9	AnM	12.8	Dioxane	none	–	80	72	> 95

[a] Expressed as percent of reactive groups reacted with the dye; nd = not determined.
[b] Run carried out in the presence of 7.75 mmol of dicyclohexylcarbodiimide.
[c] After 85 h the temperature was kept at 50 °C for 2 h.

Polymers containing carboxyl groups are used in the finishing of textiles.[2] Accordingly, SRB was reacted with NVP/MAA copolymer in DMF solution in the presence of dicyclohexylcarbodiimide and of 4-N,N-dimethylaminopyridine. After three days stirring at room temperature, only 5 % esterification was reached. Even lower dye contents were recorded when FG was used, very likely due to the low nucleophilicity of FG aromatic amino group.

In order to reach a larger degree of functionalization, SRB was reacted with the more reactive maleic anhydride/methyl vinyl ether alternating copolymer in dioxane at reflux for 48 hours. Experiments were performed in presence of *p*-toluenesulfonic acid, triethylamine, and in the absence of catalyst. Dark red polymers were obtained by this route with almost quantitative conversion of anhydride groups to the corresponding SRB hemiesters. The degree of functionalization was almost independent of the presence of a catalyst in the reaction mixture. Quantitative conversions were attained also in the reaction of the same hemiester with FG.

Use of polymeric dyes for the finishing of textiles

Preliminary dyeing experiments were performed on cotton, combed wool, and raw wool, in order to check the suitability of the prepared polymeric dyes for textile finishing. Of course, industrial processes use much more mature procedures and dyeing agents.[2,17] The fabric samples (10x10 cm squares) were kept for 1 hour in the dyeing bath at 60 °C under mild stirring. After drying in air, the fabric samples were characterized by visual inspection and by wetting measurements. The dyeing bath depletion was assessed by UV analysis (Table 3).

Table 3. Results obtained in preliminary dyeing experiments.

Dye		EtOH	Fabric		Depletion a)	Wetting time b)
type	µmol	ml	type	g	%	s
FG	106	75	Cotton	4.8	82	0.8 c)
FG	194	57	Raw wool	11.2	82	2.0
FG	106	75	Combed wool	6.7	89	2.4
FGMAm/MAA	64	50	Cotton	1.3	10	>100 c)
FGMAm/MAA	70	55	Raw wool	2.3	17	0.4
FGMAm/MAA	64	50	Combed wool	1.7	7	1.8
FGMAm/NTBAm	51	45	Cotton	1.2	6	2.6 c)
FGMAm/NTBAm	74	65	Raw wool	2.5	11	1.0
FGMAm/NTBAm	51	45	Combed wool	1.5	7	1.8

a) Evaluated by UV spectroscopy.
b) Absorption of 35% ethanol drops on the surface of dyed fabric samples.
c) Absorption of water drops.

FGMAm/MAA, and FGMAm/NTBAm copolymers containing 22 and 11% FGMAm, and FG were applied in ethanol. All dyed samples showed almost the same color, independent of dye and of adopted solvent. Of course, the commercial FG dye exhibited a much better depletion. The wettability of the treated fibers was evaluated (Table 3) by measuring the time required by a drop of water or 35% ethanol placed on the fabric surface to penetrate cotton or wool, respectively. Samples dyed with FG did not display any significant difference as compared to untreated samples. On the other hand, cotton treated with the FGMAm/MAA polymeric dye is much less hydrophilic than untreated cotton. This result confirmed that the absorbed polymer formed a rather hydrophobic surface coating on cotton fibers.

Conclusions

The reported results indicate that polymeric dyes can be prepared by copolymerization with a variety of monomers. Polymer yield, composition, distribution of monomeric units, and physical properties largely depended on the comonomer nature. Copolymerization of FGMAm with NVP or VAc gave low yields of polymers with alternating distribution of the monomeric units. On the other hand, free-radical SRBMA/NVP polymerization suggests that the SRBMA radical was not able to homopropagate the polymerization chain. Modification of preformed polymers resulted more flexible and cost effective. Moreover, this route can make use of polyfunctional dyes, although avoiding side reactions can be challenging. Indeed, reactive polymers containing significant amounts of the dye were obtained only in a few cases. However, the residual reactive groups could be exploited for the size stabilization of textiles. Very preliminary dyeing experiments indicated that the reported polymeric dyes could be used for dyeing natural fibers. Of course, getting close to the efficiency of industrial processes requires further tuning of polymer structure and improvement of the application conditions.

Acknowledgements

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