Dye-fixing Behaviors of Novel Reactive Cationic Copolymers of 3-Chloro-2-hydroxypropylmethyldiallylammonium Chloride and Dimethyldiallylammonium Chloride [P(CMDA-DMDAAC)s] on Cotton Fabric

[1,2]YIKAI YU AND [1]YUEJUN ZHANG*
[1]*School of Chemical Engineering, Nanjing, University of Science and Technology, Nanjing 210094, China.*
[2]*College of Chemistry and Chemical Engineering, Jiangxi Normal University, Nanchang 330022, China.*
yuyikai1980@163.com*

(Received on 22nd June 2012, accepted in revised form 11th September 2012)

Summary: In this article, a series of novel reactive cationic copolymers [P(CMDA-DMDAAC)s] of 3-chloro-2-hydroxypropylmethyldiallylammonium chloride (CMDA) and dimethyldiallylammonium chloride (DMDAAC) with different molecular weights characterized by intrinsic viscosities of 0.02~0.76 dL/g and different structures characterized by controlled 2%-20% molar ratios of CMDA units in main chains, were used to fix the representative reactive dyes (Reactive Scarlet 3BS and Reactive Brilliant Blue KNR) on cotton fabrics, and their dye-fixing behaviors, which were evaluated by different dye-fixing fastness such as dry rubbing fastness, wet rubbing fastness, color fastness to soaping, and white fabric staining, were studied, to develop the novel promising reactive polycationic dye-fixatives for cotton fabric. The results showed, their dye-fixing fastness was affected by their intrinsic viscosities and the molar contents of CMDA units in main chains, and those selected P(CMDA-DMDAAC)s with the intrinsic viscosities of 0.26-0.76 dL/g and 8%~20% molar contents of CMDA units in main chains, could exhibit better dye-fixing fastness and were better than all members of a group of the selected widely-used commercial polycationic dye-fixatives, which were due to the nice balance of structures and molecular weights. Thus, the selected P(CMDA-DMDAAC)s could be used as the expected novel dye-fixatives for cotton fabric.

Keywords: dye-fixing behavior; 3-chloro-2-hydroxypropylmethyldiallylammonium chloride; dimethyldiallylammonium chloride; reactive cationic copolymers; reactive unit; intrinsic viscosity; cotton fabric.

Introduction

Cotton fabric, primarily composed of cellulose, is accounting for more than 50% of total textile consumption in the world [1]. Moreover, dyed cotton must possess high colorfastness against repeated domestic launderings at 40°C–60°C [2], which is necessary to use dye-fixatives for improving the fastness properties of dyes on dyeing cotton fabrics.

From 1980s, poly (dimethyldi-allylammonium chloride) (PDMDAAC), a polymer derived from radical homopolymerization of dimethyldiallylammonium chloride (DMDAAC), has been used as the optimum polycationic dye-fixatives to enhance the uptake of anionic dyes on cotton fabric and the mechansim of interactions involved can be interpreted by the participation of electrostatic forces between the dyes and the basic cationic groups in the polymer to reduce the water solubility of dyes through the formation of color lakes [3], and the cellulose and dimethyldiallylammonium chloride have the similar units of conformational structures in main chains, which would be expected to contribute to close interactions of Van der Waals forces [4], thus, PDMDAAC dye-fixative can be widely applied for the fixing of different dyes on cotton fabrics[5~10]. However, the development about PDMDAAC-treated dyes' rubbing fastness especially wet rubbing fastness is limited, this might be due to the possible dissociation of some of color lakes based on electrostatic forces which are caused by the effect of water molecules and the interactions of Van der Waals forces between PDMDAAC and cotton fabric which are also easy to be destroyed by external forces [11]. This promotes researchers to search for new series of PDMDAAC-based dye-fixatives to further improve the fastness properties of dyes on cotton fabrics.

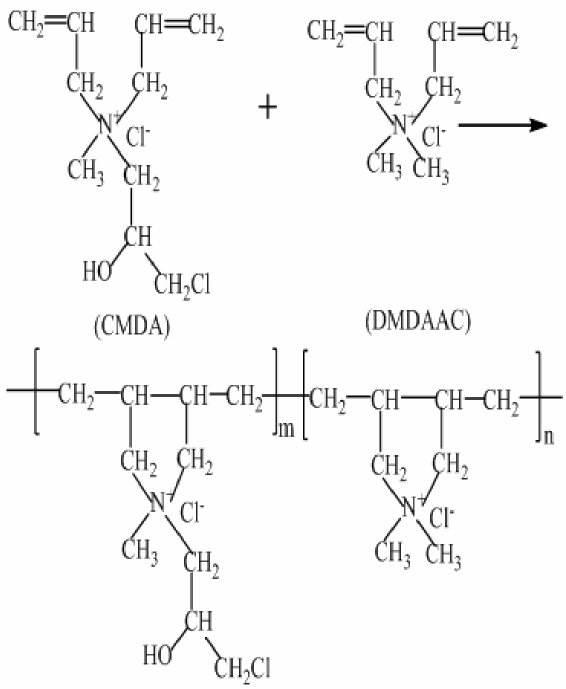
Some researches indicated that the dye-fixing performance of polycationic dye-fixatives varied from their molecular weights [12-14], and the authors discovered that those PDMDAAC dye-fixatives with the controlled molecular weights characterized by intrinsic viscosities of 0.24-0.47 dL/g could exhibit better dye-fixing performance [15]. It was suggested that their too low intrinsic viscosities would make the interactions with dyes weak, resulting in the poor dye-fixing performance and too high intrinsic viscosities would make it difficult for them to be penetrated into cotton

***To whom all correspondence should be addressed.**

fabrics to interact with dyes, again resulting in the poor dye-fixing performance. Therefore their suitable molecular weights should be controlled. In addition, if small molar percentages (less than 20%) of reactive units, which can bring about the crosslinking reactions with the hydroxyl groups of cotton (cellulose) to form a covering film on cotton surface, are incorporated into the backbones of PDMDAAC, the dye-fixing performance of those modified PDMDAAC can also be improved [16]. In view of these points, in previous work, a series of novel reactive cationic copolymers of CMDA and DMDAAC [P(CMDA-DMDAAC)s] (PDMDAAC-based dye-fixatives) with controlled 2%-20% molar ratios of CMDA units in main chains and controlled molecular weights characterized by intrinsic viscosities of 0.15~0.76 dL/g, which were designed as more useful PDMDAAC-based dye-fixatives and derived from the further incorporation of controlled contents (below 20% molar contents) of reactive units (CMDA units) into the backbones of the molecular-weight-controlled PDMDAAC with the controlled intrinsic viscosities of 0.24-0.47 dL/g or nearly, were successfully synthesized (Scheme 1) [17]. Thus, in this article, on the basis of the fixing fundamentals of reactive dye-fixatives on cotton fabric [16], these novel cationic copolymers of P (CMDA-DMDAAC)s were further used to fix the anionic dyes on cotton fabrics, and their dye-fixing behaviors were discussed in detail, to obtain the novel promising reactive polycationic dye-fixatives for cotton fabric.

Results and Discussion

Based on our previous contribution [17], a series of novel P(CMDA-DMDAAC)s with controlled 2%-20% molar contents of CMDA units in main chains and controlled intrinsic viscosities of 0.02~0.76 dL/g were synthesized according to the copolymerization of 3-chloro-2-hydroxypropyl-methyldiallylammonium chloride (CMDA) and dimethyldiallylammonium chloride (DMDAAC) and by varying molar ratios of raw materials of CMDA to DMDAAC from 1/99 to 20/80 and increasing initial monomer concentrations from 19% to 40% with the decrease of initiator amount from 12% to 6% during polymerization. In this article, the obtained P(CMDA-DMDAAC)s with different intrinsic viscosities and structures were used to fix the selected anionic dyes (Reactive Scarlet 3BS and Reactive Brilliant Blue KNR) dyed on the cotton fabrics, and their dye-fixing behaviors were studied in detail, which were all evaluated by the different dye-fixing fastness of P(CMDA-DMDAAC) s [i.e., the color fastness of anionic dyes on the dyeing cotton fabrics after being fixed by P(CMDA-DMDAAC) s], such as dry rubbing fastness, wet rubbing fastness, color fastness to soaping, and white fabric staining.



Scheme-1: Preparation of novel cationic copolymers of P (CMDA-DMDAAC) s in previous work.

Dye-Fixing Behaviors of P(CMDA-DMDAAC)s at Normal Fixing Temperatures

Research Results on Dye-Fixing Behaviors of P(CMDA-DMDAAC)s at Normal Fixing Temperatures

The obtained P(CMDA-DMDAAC)s with different intrinsic viscosities and structures were used to fix the Reactive Scarlet 3BS and Reactive Brilliant Blue KNR dyed on the cotton fabrics at normal fixing temperatures (60 ℃), for investigating their dye-fixing behaviors (or dye-fixing fastness) on cotton fabrics, the results were given in Table-1.

The results showed, their dye-fixing fastness was affected by their different intrinsic viscosities and molar ratios of CMDA units.

Table-1: Dye-fixing fastness of P(CMDA-DMDAAC)s at normal temperatures (60 ℃).

Sample*	$n_{(CMDA)}/n_{(DMDAAC)}$	Intrinsic viscosity ($dL \cdot g^{-1}$)	Cotton fabrics dyed with Reactive Scarlet 3BS				Cotton fabrics dyed with Reactive Brilliant Blue KNR			
			Dry rubbing fastness	Wet rubbing fastness	White fabric staining	fastness to soaping	Dry rubbing fastness	Wet rubbing fastness	White fabric staining	fastness to soaping
1	2/98	0.19	4	3-4	4-5	4-5	4-5	3-4	4-5	4-5
2	2/98	0.22	3-4	3	4-5	4-5	4-5	3-4	4-5	4-5
3	2/98	0.26	4	3	4-5	4-5	4-5	3	4-5	4-5
4	2/98	0.37	4	3-4	4-5	4-5	4-5	3-4	4-5	4-5
5	2/98	0.40	4	3	4-5	4-5	4-5	3-4	4-5	4-5
6	2/98	0.49	4-5	3-4	4-5	4-5	4	3-4	4-5	4-5
7	4/96	0.16	4	3	4-5	4-5	4-5	3-4	4-5	4-5
8	4/96	0.20	3-4	2-3	4-5	4-5	4	3-4	4-5	4-5
9	4/96	0.24	3-4	3	4-5	4-5	4-5	3-4	4-5	4-5
10	4/96	0.28	3-4	3	4-5	4-5	4-5	3-4	4-5	4-5
11	4/96	0.39	4	3-4	4-5	4-5	4-5	3-4	4-5	4-5
12	4/96	0.46	3-4	3	4-5	4-5	4-5	3-4	4-5	4-5
13	4/96	0.57	4	3-4	4-5	4-5	4-5	3-4	4-5	4-5
14	6/94	0.17	3-4	3	4-5	4-5	4-5	3-4	4-5	4-5
15	6/94	0.20	4	3	4-5	4-5	4-5	3	4-5	4-5
16	6/94	0.25	4	3-4	4-5	4-5	4-5	3-4	4-5	4-5
17	6/94	0.28	4	3-4	4-5	4-5	4-5	3	4-5	4-5
18	6/94	0.41	4	3	4-5	4-5	4-5	3	4-5	4-5
19	6/94	0.55	4	3-4	4-5	4-5	4-5	3-4	4-5	4-5
20	8/92	0.17	3-4	3-4	4-5	4-5	4-5	3-4	4-5	4-5
21	8/92	0.26	4	3-4	4-5	4-5	4-5	4	4-5	4-5
22	8/92	0.32	4	3-4	4-5	4-5	4-5	3-4	4-5	4-5
23	8/92	0.50	4	3-4	4-5	4-5	4-5	4	4-5	4-5
24	10/90	0.02	4	3	4-5	4-5	4-5	3	4-5	4-5
25	10/90	0.07	4	3	4-5	4-5	4-5	3-4	4-5	4-5
26	10/90	0.16	4	3-4	4-5	4-5	4-5	3-4	4-5	4-5
27	10/90	0.37	4	3-4	4-5	4-5	4-5	4	4-5	4-5
28	10/90	0.69	4	3-4	4-5	4-5	4-5	4	4-5	4-5
29	20/80	0.04	3-4	3	4-5	4-5	4-5	3	4-5	4-5
30	20/80	0.08	3-4	3	4-5	4-5	4-5	3	4-5	4-5
31	20/80	0.15	3-4	3-4	4-5	4-5	4-5	3-4	4-5	4-5
32	20/80	0.23	4	3-4	4-5	4-5	4-5	3-4	4-5	4-5
33	20/80	0.76	3-4	3-4	4-5	4-5	4-5	3-4	4-5	4-5
LYPF	0/100	0.59	4	3	4-5	4-5	4-5	3	4-5	4-5
PDAC	0/100	0.58	4	3	4-5	4-5	4-5	3	4-5	4-5
Fix		0.067	4	3-4	4-5	4-5	4-5	3-4	4-5	4-5
PDMDAAC	0/100	0.41	4	3-4	4-5	4-5	4-5	3-4	4-5	4-5
Bank			3-4	3	4	4	4	3	4	4

(*) The information of all the samples was described as Section 2.1.

Effect of Intrinsic Viscosities on Dye-Fixing Fastness of P(CMDA-DMDAAC)s

Table-1 showed, at the same molar ratios of CMDA units in main chains, the dye-fixing performance of obtained P(CMDA-DMDAAC)s varied according to their different intrinsic viscosities. For example, the dye-fixing performance of Samples 24~28 with the same 10% molar ratios of CMDA units in main chains, varied with regard to their different intrinsic viscosities. Among them, Samples 27~28 with intrinsic viscosities of 0.37~0.69 dL/g, exhbit better dye-fixing fastness, however, Samples 24~26 with intrinsic viscosities of 0.02~0.16 dL/g, exhibited poorer dye-fixing fastness. This might be due to some possessing intrinsic viscosities of too low which would make the interactions between P(CMDA-DMDAAC)s and dyes weak, resulting in the poor dye-fixing fastness. Conversely, if the intrinsic viscosities were too high, this would make it difficult for them to be penetrated into cotton fabrics to interact with dyes, also resulting in the poor dye-fixing fastness [15].

Keeping the above-mentioned general considerations regarding the effect of intrinsic viscosities on the dye-fixing performance, those P(CMDA-DMDAAC)s possessing intrinsic viscosities in the 0.25~0.69 dL/g range could stably exhibit better dye-fixing fastness.

Effect of Structures on Dye-Fixing Fastness of P(CMDA-DMDAAC)s

Table-1 also showed, with the similar intrinsic viscosities, the dye-fixing fastness of obtained P(CMDA-DMDAAC)s varied according to their different molar ratios of CMDA units in main chains, for example, the dye-fixing fastness of Samples (3, 9, 16, and 21) with the similar intrinsic viscosities of 0.24~0.26 dL/g, varied with respect to their different structure-units' compositions in main chains, among them, Sample 21 with 8% CMDA units in main chains exhibited a better dye-fixing fastness, however, other samples (3, 9, and 16) exhibited poorer dye-fixing fastness. This might be due to their possessing too low contents of reactive units making their reactions with cotton fabric very weak, resulting in the poor dye-fixing performance, but too high contents of reactive units would make the similar conformational interactions of cellulose and DMDAAC units become weak, also resulting in the poor dye-fixing fastness [18].

Keeping the above-mentioned general considerations regarding the effect of structures on the dye-fixing fastness, those P(CMDA-DMDAAC)s with the 8%~10% molar ratios of CMDA units in main chains could stably exhibit better dye-fixing fastness.

Combined Effect of Intrinsic Viscosities and Structures on Dye-Fixing Fastness of P(CMDA-DMDAAC)s

Generally, the results in Table-1 showed, those P(CMDA-DMDAAC)s with the intrinsic viscosities of 0.26-0.69 dL/g and 8%~10% molar ratios of CMDA units in main chains tended to exhibit better dye-fixing fastness at normal fixing temperature (60 ℃) due to the nice balance between their structures and intrinsic viscosities.

Compared to blank values, the dye-fixing fastness of those P(CMDA-DMDAAC)s with the intrinsic viscosities of 0.26-0.69 dL/g and the 8%~10% CMDA-units' molar ratios in main chains was improved 0.5~1 grades.

Moreover, those P(CMDA-DMDAAC)s' better wet rubbing fastness was 0.5~1 grades better than commercial PDMDAAC dye-fixatives of Dye-fixative LYPF and Dye-fixative PDAC, and was near to the selected molecular-weight-controlled PDMDAAC and the commercial polycationic Dye-fixative Fix.

In addition, the color fastness (especially the wet rubbing fastness) of Reactive Brilliant Blue KNR fixed by those P(CMDA-DMDAAC)s with the intrinsic viscosities of 0.26-0.69 dL/g and the 8%~10% CMDA-units' molar ratios in main chains appeared to be slightly better than that of Reactive Scarlet 3BS under the same fixing conditions, because there was a lower contents (just two) of sulfonate anion in the structure of Reactive Brilliant Blue KNR than those of Reactive Scarlet 3BS, possibly resulting in the higher water resistance of the color lakes derived from the fixing interactions of the Reactive Brilliant Blue KNR with P(CMDA-DMDAAC)s in turn. Moreover, the amine groups of Reactive Brilliant Blue KNR could bring about the effective linking reactions with the 3-chloro-2-hydroxy propyl groups of P(CMDA-DMDAAC)s, also possibly resulting the higher color fastness.

Dye-Fixing Behaviors of P(DHAC-DMDAAC)s at Higher After-Treating Temperatures

Effect of Different Higher after Treating Temperatures on Dye-Fixing Fastness of P(CMDA-DMDAAC)s

The effect of different commonly-used higher after-treating temperatures (120 ℃, 140 ℃, 160 ℃, and 180℃) on the wet rubbing fastness of one P(CMDA-DMDAAC)-fixed cotton fabric dyed with Reactive Scarlet 3BS was studied as one example [16], to get the suitable after-treating temperature, the result was given in Fig. 1.

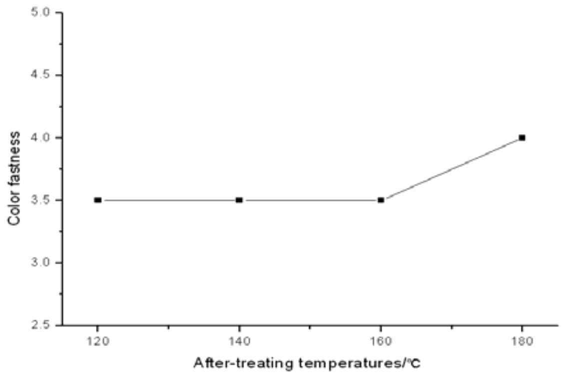


Fig. 1: The effect of different after-treating temperatures on one P(CMDA-DMDAAC)'s wet rubbing fastness (Sample 32).

Fig. 1 showed, when the after-treating temperature was increased from 120 ℃ to 160 ℃, the wet rubbing fastness of Sample 28 changed a little, however, when the after-treating temperature was further increased to 180 ℃, the wet rubbing fastness could further improved from 3~4 grades to 4 grades (In Fig. 1, 3.5 grades were representative of 3~4 grades), indicating that the suitable after-treating temperature might be 180 ℃. Moreover, no decrease of the initial decomposition temperature of the P(CMDA-DMDAAC)-treated cotton sample at 180 ℃, was happened in the TGA analysis (Fig. 2), confirming the stability of treated fabrics after treatment in this range of temperature.

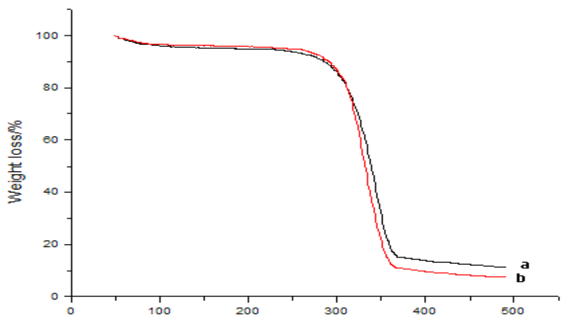


Fig. 2: A analysis of untreated cotton sample and P(CMDA-DMDAAC)-treated cotton sample.
(a) Untreated cotton sample, (b) P(CMDA-DMDAAC)-treated cotton sample.

Dye-Fxing Bhaviors of P(CMDA-DMDAAC)s at Hgher after-Teating Tmperatures

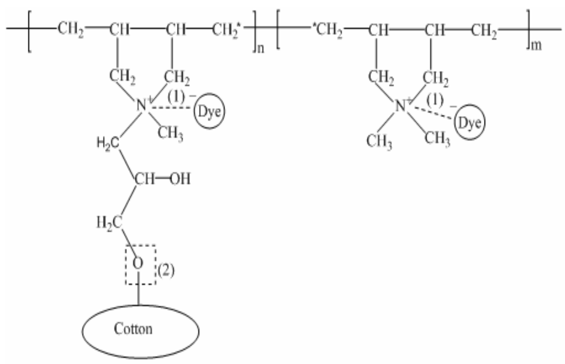
Research Rsults on De-Fixing Behaviors of P(CMDA-DMDAAC)s at Higher after-Treating Temperatures

All the fixed cotton fabrics dyed with Reactive Scarlet 3BS or Reactive Brilliant Blue KNR were further treated at 180 ℃ for 3 min, to investigate their dye-fixing behaviors (or dye-fixing fastness) at higher after-treating temperature (180 ℃), the results were shown in Table-2.

Compared to the results in Table-1, the results in Table-2 showed, the dye-fixing fastness would vary from the new effect of the intrinsic viscosities and molar ratios of CMDA units in main chains of P(CMDA-DMDAAC)s at higher after-treating temperatures.

The New Effect of Intrinsic Viscosities and Structures on Dye-Fixing Fastness at Higher after-Treating Temperatures

Compared to the results in Table-1, the results in Table-2 showed, the dye-fixing fastness (especially the wet rubbing fastness) of the obtained P(CMDA-DMDAAC)s with above 8% CMDA-units' molar ratios in main chains tended to be further improved after being treated at 180 ℃ due to the reactive units (CMDA units) which could possibly bring about the effective linking reactions with the hydroxyl groups of cotton (cellulose) to form a covering film on cotton surface for improving the fastness of dyes on cotton, and play a role in the further development of fastness of dyes at higher temperature (Scheme 5), which would be according to the fixing fundamentals of reactive dye-fixatives on cotton fabric [16].



Scheme-2: Possible dye-fixing model of P(CMDA-DMDAAC)s and dyeing cotton fabric baked at higher temperatures (180 ℃).
(1) Formation of color lakes; (2) further linking interactions of P(CMDA-DM)s and cotton fabric.

However, the blank values of fastness of dyes on unfixed dyeing-cotton samples and the dye-fixing fastness of the selected molecular-weight-controlled PDMDAAC, commercial polycationic PDMDAAC dye-fixatives (Dye-fixative LYPF, Dye-fixative PDAC) and cationic Dye-fixative Fix changed a little after being treated at 180 ℃, because the effect of direct interactions between reactive dyes and cotton fibres was very limited and there were no reactive units in those polycationic main chains which could possibly bring about the effective linking reactions with the hydroxyl groups of cotton (cellulose).

Table-2: Dye-fixing fastness of P(CMDA-DMDAAC)s baked at higher temperatures (180 ℃).

Sample*	$n_{(CMDA)}/n_{(DMDAAC)}$	Intrinsic viscosity ($dL{\cdot}g^{-1}$)	Cotton fabrics dyed with Reactive Scarlet 3BS				Cotton fabrics dyed with Reactive Brilliant Blue KNR			
			Dry rubbing fastness	Wet rubbing fastness	White fabric staining	fastness to soaping	Dry rubbing fastness	Wet rubbing fastness	White fabric staining	fastness to soaping
1	2/98	0.19	4	3	4-5	4-5	4	3-4	4-5	4-5
2	2/98	0.22	4	3-4	4-5	4-5	4	3	4-5	4-5
3	2/98	0.26	4	3-4	4-5	4-5	4	3-4	4-5	4-5
4	2/98	0.37	4	3-4	4-5	4-5	4-5	3-4	4-5	4-5
5	2/98	0.40	4	3	4-5	4-5	4-5	3-4	4-5	4-5
6	2/98	0.49	4	3-4	4-5	4-5	4	3-4	4-5	4-5
7	4/96	0.16	3-4	3	4-5	4-5	4	3-4	4-5	4-5
8	4/96	0.20	4	3	4-5	4-5	4-5	3-4	4-5	4-5
9	4/96	0.24	3-4	3-4	4-5	4-5	4-5	3-4	4-5	4-5
10	4/96	0.28	4-5	3-4	4-5	4-5	4	3-4	4-5	4-5
11	4/96	0.39	4	3-4	4-5	4-5	4-5	3-4	4-5	4-5
12	4/96	0.46	4	3	4-5	4-5	4	3-4	4-5	4-5
13	4/96	0.57	3-4	3-4	4-5	4-5	4-5	3-4	4-5	4-5
14	6/94	0.17	4	3-4	4-5	4-5	4	3-4	4-5	4-5
15	6/94	0.20	3-4	3-4	4-5	4-5	4-5	3	4-5	4-5
16	6/94	0.25	4	3-4	4-5	4-5	4-5	3-4	4-5	4-5
17	6/94	0.28	4-5	3-4	4-5	4-5	4	3	4-5	4-5
18	6/94	0.41	4	3-4	4-5	4-5	4-5	3	4-5	4-5
19	6/94	0.55	4	3-4	4-5	4-5	4-5	3-4	4-5	4-5
20	8/92	0.17	4	3-4	4-5	4-5	4-5	3-4	4-5	4-5
21	8/92	0.26	4-5	4	4-5	4-5	4-5	4	4-5	4-5
22	8/92	0.32	4-5	4	4-5	4-5	4-5	4	4-5	4-5
23	8/92	0.50	4-5	4	4-5	4-5	4-5	4	4-5	4-5
24	10/90	0.02	4	3-4	4-5	4-5	4-5	3-4	4-5	4-5
25	10/90	0.07	4	3-4	4-5	4-5	4-5	3-4	4-5	4-5
26	10/90	0.16	4	4	4-5	4-5	4-5	4	4-5	4-5
27	10/90	0.37	4	4	4-5	4-5	4-5	4	4-5	4-5
28	10/90	0.69	4	4	4-5	4-5	4-5	4	4-5	4-5
29	20/80	0.04	4	3-4	4-5	4-5	4-5	3-4	4-5	4-5
30	20/80	0.08	4	3-4	4-5	4-5	4-5	3-4	4-5	4-5
31	20/80	0.15	4	4	4-5	4-5	4-5	4	4-5	4-5
32	20/80	0.23	4	4	4-5	4-5	4-5	4	4-5	4-5
33	20/80	0.76	4-5	4	4-5	4-5	4-5	4	4-5	4-5
LYPF	0/100	0.59	4	3	4-5	4-5	4-5	3	4-5	4-5
PDAC	0/100	0.58	4	3	4-5	4-5	4-5	3	4-5	4-5
Fix		0.067	4	3-4	4-5	4-5	4-5	3-4	4-5	4-5
PDMDAAC	0/100	0.41	4	3-4	4-5	4-5	4-5	3-4	4-5	4-5
Bank			3-4	3	4	4	4	3	4	4

(*) The information of all the samples was described as Section 2.1.

Moreover, samples with the intrinsic viscosities of 0.15-0.76 dL/g and 8%~20% molar ratios of CMDA units in main chains were found to exhibit best dye-fixing fastness due to the new nice balance of structures and molecular weights, and the dye-fixing fastness on treating the cotton fabrics dyed with Reactive Scarlet 3BS or Reactive Brilliant Blue KNR was listed as follows: all the dry rubbing fastness reached above 4 grades, all the wet rubbing fastness reached 4 grades, all the color fastness to soaping reached 4~5 grades, and all the white fabric staining reached 4~5 grades.

Compared to blank values, the dye-fixing fastness of those P(CMDA-DMDAAC)s with the intrinsic viscosities of 0.15-0.76 dL/g and 8%~20% molar ratios of CMDA units in main chains was improved 0.5~1 grades, especially the wet rubbing fastness properties were improved 1 grades.

In addition, the dye-fixing fastness of the those P(CMDA-DMDAAC)s with the intrinsic viscosities of 0.15~0.76 dL/g and 8%~20% molar ratios of CMDA units in main chains was better than that of the selected molecular-weight-controlled PDMDAAC, indicating that the dye-fixing fastness of those PDMDAAC-based dye-fixatives could be further developed by incorporation of 8%~20% molar ratios of CMDA units into the main chains of molecular-weight-controlled poly (dimethyldiallylammonium chloride) (PDMDAAC) dye-fixatives.

Fatherly, the dye-fixing fastness of the those P(CMDA-DMDAAC)s with the intrinsic viscosities of 0.15~0.76 dL/g and 8%~20% molar ratios of CMDA units in main chains was better than that of all the selected widely-used commercial polycationic dye-fixatives (Dye-fixative LYPF, Dye-fixative PDAC, and Dye-fixatives Fix), especially, those wet rubbing fastness of P(CMDA-DMDAAC)s was 1 grades better than commercial PDMDAAC dye-fixatives of Dye-fixative LYPF and Dye-fixative PDAC, and was 0.5 grades better than the commercial polycationic Dye-fixative Fix.

Thus, those P(CMDA-DMDAAC)s with the intrinsic viscosities of 0.26-0.76 dL/g and 8%~20% molar ratios of CMDA units in main chains could be used as the expected novel dye-fixatives on cotton fabric.

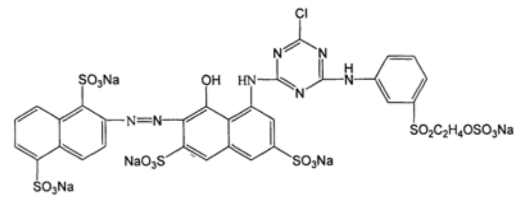
Experimental

Materials

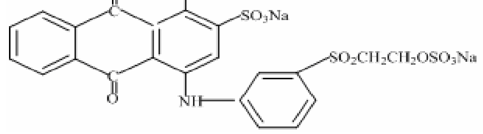
A series of novel P(CMDA-DMDAAC)s with controlled 2%-20% molar ratios of CMDA units in main chains and controlled intrinsic viscosities of 0.02~0.76 dL/g were synthesized by copolymerizing 3-chloro-2-hydroxypropylmethyl-diallylammonium chloride (CMDA) and dimethyldiallylammonium chloride (DMDAAC), varying molar ratios of raw materials of CMDA to DMDAAC from 1/99 to 20/80 and increasing the initial monomer concentrations from 19% to 40% while decreasing of initiator amount from 12% to 6% during polymerization in the literature [17]. The mentioned PDMDAAC with controlled molecular weights represented by an intrinsic viscosity of 0.41 dL/g was synthesized by the homo-polymerization of dimethylammonium chloride at 60 ℃ for 6 h and then ripening at 70 ℃ for 2 h when the initial monomer concentration (w/w) was 52.5% and 3% initiator (w/w) according to the previous contribution [15]. Reactive Scarlet 3BS (industrial Purity) and Brilliant Blue KNR (industrial Purity) were collected and stored over sieves. Dye-fixative LYPF (PDMDAAC dye-fixative, industrial Purity) was purchased from Shangdong Luyue Chemical Co., Ltd (China) and used directly without any treatment. Dye-fixative PDAC (PDMDAAC dye-fixative, industrial Purity) was purchased from Jiangsu Feixiang Chemical Co., Ltd (China) and used directly without any treatment. Dye-fixative Fix (cationic dye-fixative, industrial Purity) was purchased from BASF Chemical Co., Ltd (German) and used directly without any treatment. Cotton fabric (industrial Purity) was collected from Jiangsu Nantong Si'ente Chemical Co., Ltd (China) and used directly without any treatment.

Dye-Fixing Behaviors of P(CMDA-DMDAAC)s

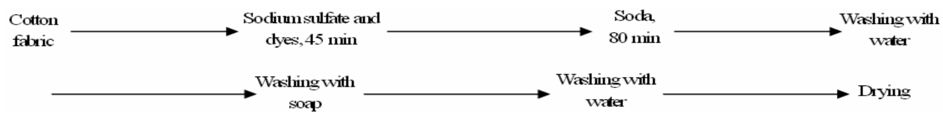
According to current widely-used dyeing and fixing processes [12~15], the cotton fabric was first dyed at 60 ℃ with 2% (o.w.f) some representative reactive dyes which are usually difficult to use for coloring on cotton fabric, such as Reactive Scarlet 3BS (Scheme 3) or Brilliant Blue KNR (Scheme 4), as shown in Scheme 5. Then 3% (o.w.f) of P(CMDA-DMDAAC)s were used to fix the selected anionic dyes dyed on the cotton fabrics at 60 ℃ for 30 min, the pH of fix application was 7, the liquor ratio was 1 :20, and then some of the fixed dyeing cotton samples were dried and the dye-fixing behaviors of P(CMDA-DMDAAC)s at normal temperatures was investigated, which were all evaluated by different dye-fixing fastness of P(CMDA-DMDAAC) s such as dry rubbing fastness, wet rubbing fastness, color fastness to soaping, and white fabric staining. Similarly, some of another above-mentioned fixed dyeing cotton samples were further baked at 180 ℃ for 3 min, for investigating the dye-fixing behaviors of P(CMDA-DMDAAC)s baked at higher temperatures, after the effect of different commonly-used higher after-treating temperatures (120 ℃, 140 ℃, 160 ℃, and 180℃) on the wet rubbing fastness of the P(CMDA-DMDAAC)-fixed cotton fabric dyed with Reactive Scarlet 3BS was studied [16]. Moreover, in order to get the objective appraisal of P(CMDA-DMDAAC)s' dye-fixing performance, the blank values of fastness of dyes on unfixed dyeing-cotton samples and the dye-fixing fastness of one PDMDAAC controlled molecular weights represented by intrinsic viscosity of 0.41 dL/g (as one example), the widely-used commercial PDMDAAC dye-fixatives (Dye-fixative LYPF, Dye-fixative PDAC) and widely-used polyationic Dye-fixative Fix were also investigated under the same designed fixing processes, which was used to be compared with those of P(CMDA-DMDAAC)s.



Scheme-3: Structure of Reactive Scarlet 3BS.



Scheme-4: Structure of Brilliant Blue KNR.



Scheme-5: Dyeing of cotton fabric.

Measurement

The dry rubbing fastness and wet rubbing fastness represented by different color fastness grades (i.e., grades 1~5), were measured using a rubbing fastness instructment (YB872) according to ISO 105-X12: 2001, MOD. Fixed cotton samples which were attached with white fabrics (4 cm × 10 cm), were washed in 50 ml soap solutions at 60 ℃ for 30 min to test the color fastness to soaping and white fabric staining according to ISO 105-C10: 2006, MOD, both of which were represented by different color fastness grades (i.e., grades 1~5). Thermogravimetric analysis (TGA) was carried out on a Perkn-Elmer 7 Series thermal analysis system with an increasing rate of 10 ℃/min, N_2 atmosphere at the flow rate of 40 ml/min, scanning scope ranging from 50 to 500 ℃,and sample weight of 5.0~7.0 mg.

Conclusions

A series of novel reactive cationic copolymers [P(CMDA-DMDAAC)s] of 3-chloro-2-hydroxypropylmethyldiallylammonium chloride and dimethyldiallylammonium chloride were used to fix the anionic dyes on cotton fabrics, and their dye-fixing behaviors were studied in details. The possible conclusions could be drawn as follows:

(1) Those P(CMDA-DMDAAC)s with the intrinsic viscosities of 0.26-0.69 dL/g and the 8%~10% molar ratios of CMDA units in main chains tended to exhibit better dye-fixing fastness at normal fixing temperature (60 ℃) due to the nice balance between their structures and intrinsic viscosities.

(2) The dye-fixing fastness of the selected P(CMDA-DMDAAC)s with above 8% molar ratios of CMDA units in main chains tended to be further improved after being treated at 180 ℃ due to the reactive units (CMDA) which could possibly bring about the effective linking reactions with the hydroxyl groups of cotton (cellulose) to form a covering film on cotton surface for improving the fastness of dyes on cotton, and play a role in further development of the fastness of dyes.

(3) Those P(CMDA-DMDAAC)s with the intrinsic viscosities of 0.15-0.76 dL/g and 8%~20% molar ratios of CMDA units in main chains were found to exhibit the best dye-fixing fastness due to the new nice balance between structures and intrinsic viscosities at higher temperatures (180 ℃). Their performances were better than any of the widely-used commercial polycationic dye-fixatives selected, and they could be used as the expected novel dye-fixatives for cotton fabric.

References

1. H. F. Wang, Y. Y. Cheng and H. Lin, *Journal of Soochow University (engineering science edition)*, **23**, 12 (2003).
2. J. Zhang, *Fine and Specialty Chemicals*, **12**, 1 (2004).
3. C. Wandrey, B. J. Hernandez and D. Hunkerler, *Advanced Polymer Science*, **145**, 123 (1999).
4. S. Rosunee and C. M. Carre, *Journal of Materials Science*, **38**, 2179 (2003).
5. R. S. Blackburn and S. M. Burkinshaw, *Journal of Applied Polymer Science*, **89**, 1026 (2003).
6. S. M. Burkinshaw and A. Gotsopoulos, *Dyes and Pigments*, **42**, 179 (1999).
7. S. M. Burkinshaw and A. Gotsopoulos, *Dyes and Pigments*, **32**, 209 (1996).
8. K. Shinbo, K. Onishi and S. Miyabayashi, *Thin Solid Films*, **438**, 177 (2003).
9. G. Nizri, S. Lagerge and A. Kamyshny, *Journal of Colloid and Interface Science*, **320**, 74 (2008).
10. S. M. Burkinshaw, D. Katsarelias, *Dyes and Pigments*, **29**, 139 (1995).
11. X. Zhang, B. Mao and M. H. Xiang, *Textile Auxiliaries*, **22**, 5 (2005).
12. W. Li, H. Hong and H. Zhang, *Journal of Beijing Institute of Clothing Technology*, **28**, 19 (2008).
13. K. Komiya, S. Kanai and K. Beppu, *Japan Patent*, **63**, 264 (1988).
14. J. G. ZHANG, *Fine Petrochemical Industry*, **1**, 36 (1992).
15. Y. K. Yu and Y. J. Zhang, *Journal of Vinyl and Additive Technology*, **16**, 277 (2010).
16. H. T. Yang, X. D. Zhou and J. Dong, *Dye Printing*, **5**, 10 (2010).
17. Y. K. Yu and Y. J. Zhang, *Research on Chemical Intermediates*, DOI: 10.1007/s11164-012-0529-6 (In Press, 2012).
18. Y. K. Yu and Y. J. Zhang, *Journal of Textile Research*, **31**, 145 (2010).