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DYE-FIXING PERFORMANCES OF SLIGHTLY CROSS-LINKED POLY (DIMETHYLDIALLYLAMMONIUM CHLORIDES) ON COTTON FABRIC

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Slightly cross-linked poly (dimethyldiallylammonium chlorides) (PDMDAACs) with different molecular weights characterized by intrinsic viscosities and structures were prepared as copolymers of triallylmethylammonium chloride (TAMAC), a cross-linking monomer, with dimethyldiallylammonium chloride (DMDAAC). They were then studied as novel, promising reactive polycationic dye-fixatives on cotton fabric. A series of slightly cross-linked PDMDAACs with controlled 1–5% molar ratios of crosslinking units (TAMAC units) in the main chains and intrinsic viscosities of 0.04–0.86 dl/g were used to treat cotton fabrics dyed with anionic dyes such as Reactive Scarlet 3BS and Reactive Brilliant Blue KNR. Their dye-fixing performance, evaluated by dry rubbing fastness, wet rubbing fastness, colour fastness to soaping, and white fabric staining, were examined. The results showed their dye-fixing performances were affected by their intrinsic viscosities and the molar content of TAMAC units; slightly cross-linked PDMDAACs with intrinsic viscosities of 0.16–0.30 dl/g and 1% TAMAC exhibited the best dye-fixing performances and were better than all members of a group of selected widely-used commercial polycationic dye-fixatives. This was attributed to their plane-like structures and the nice balance between structure and intrinsic viscosities. Thus it was confirmed that the selected slightly cross-linked PDMDAACs can be used as novel dye-fixatives on cotton fabric.

Keywords: triallylmethylammonium chloride; dimethyldiallylammonium chloride; copolymers; slightly cross-linking; intrinsic viscosity; dye-fixatives; dye-fixing performance

ПЕРФОРМАНСИ ЗА ФИКСИРАЊЕ НА БОЈАТА НА СЛАБО ВМРЕЖЕНИ ПОЛИ(ДИМЕТИЛДИАЛИЛАМОНИУМ ХЛОРИДИ) НА ПАМУЧЕН МАТЕРИЈАЛ

Беа подготвени слабо вмрежени поли(диметилдиалиламониум хлориди) (PDMDAAC) со различни молекулски маси со специфична вискозност и структура како кополимери на триалил-метиламониум-хлорид (TAMAC) како мономер за вмрежување со диметилдиалиламониум хлорид (DMDAAC). Тие претставуваат нови погодни реактивни поликатјонски фиксири на боја за памучен материјал. Во испитувањата беше користена серија од слабо вмрежени PDMDAAC со контролирани молски односи од 1–5% на мономер за вмрежување (TAMAC) во главните низи и со внатрешна вискозност од 0,04–0,86 dl/g за третирање на памучен материјал обоен со анјонска боја *Reactive Scarlet 3B*S или *Reactive Brilliant Blue KNR.* Беа испитувани нивните особини за фиксирање според брзината на обезбојување, сушење, обојување, сапонификација и белење. Резултатите покажуват дека особините за фиксирање на бојата зависат од внатрешната вискозност и моларната содржина на кополимерот TAMAC; слабо вмрежените PDMDAAC со внатрешни густини од 0,16–0,30 dl/g и

1% TAMAC покажуваат најдобри особини на боење и беа подобри од сите претставници на групата на познати комерцијални поликатјонски фиксири на бои. Овие особини се резултат на нивните приближно плочести струтури и задоволителната рамнотежа помеѓу структурните особини и вискозноста. Така беше потврдено дека слабо вмрежените PDMDAAC можат да се применуваат како нови фиксири на боја за памучни ткаенини.

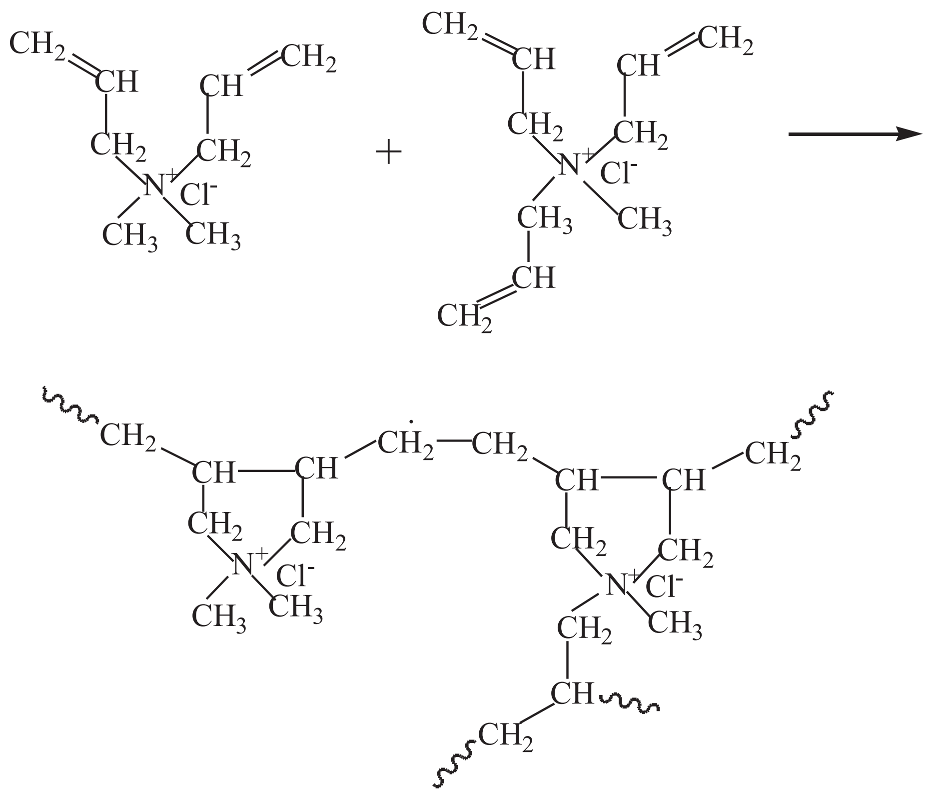
Клучни зборови: кополимери; триалилметиламониум хлорид; диметилдиалиламониум хлорид; слабо вмрежување; внатрешна вискозност; фиксири на бои; особини за боење

1. INTRODUCTION

Cotton fabric, primarily composed of cellulose, is widely used in the world, accounting for more than 50% of total textile consumption [1]. Dyed cotton should possess high colour fastness against repeated domestic launderings [2].

At present, poly(dimethyldiallylammonium chloride) (PDMDAAC), a polymer derived from radical homopolymerization of dimethyldiallylammonium chloride (DMDAAC) [3], has been used as the optimum polycationic dye-fixative to improve the colour fastness properties of different anionic dyes on cotton fabric. The mechanism of the interactions involved can be interpreted in terms of the participation of electrostatic forces between the free anionic dyes and the cationic groups in the polymer to reduce the water solubility of dyes through the formation of colour lakes [4]. In addition, cellulose and dimethyldiallylammonium chloride have units of similar conformation in their main chains, which would be expected to contribute to close interactions of Van der Waals forces [5]. Thus, PDMDAAC dye-fixative has been widely applied for the fixing of different dyes in cotton fabric [6–11]. However, PDMDAAC usually exhibits poor rubbing fastness, in particular poor wet rubbing fastness. This might be due to the dissociation of some colour lakes based on electrostatic forces, which are easily destroyed by the effect of water molecules. In addition, the interactions of Van der Waals forces between PDMDAAC and cotton fabric are also easily disrupted by external forces [12]. This has promoted researchers to search for new series of PDMDAAC-based dye-fixatives to further improve the fastness performances of dyes on cotton fabrics.

Some research has indicated that the dye-fixing properties of polycationic dye-fixatives are affected by their molecular weights [13–15]. In one report, PDMDAAC dye-fixatives with controlled molecular weights characterized by intrinsic viscosities of 0.24–0.47 dl/g were discovered to exhibit improved dye-fixing performances [16]. It was suggested that their interactions with dyes would be very weak when the intrinsic viscosities were too low, resulting in poor dye-fixing performances, and they would also have great difficulty penetrating into cotton fabrics to interact with the dyes when the molecular weights were too high, again resulting in poor dye-fixing performances. Therefore their molecular weights should be controlled. On the other hand, if a small molar percentage (less than 5%) of crosslinking units was incorporated into the backbones of PDMDAACs, the dye-fixing performances of these slightly cross-linked PDMDAACs was also improved, due to the plane-like nature of the crosslinking structures, which expanded the interactions with dyes, again resulting in improved dye-fixing performances [17, 18]. In view of these points, in previous work a series of slightly cross-linked PDMDAACs (PDMDAAC-based dye-fixatives) with less than 5% TAMAC crosslinking units and controlled intrinsic viscosities of 0.24–0.47 dl/g, or nearly, were successfully synthesized as copolymers of 1%–5% triallylmethylammonium chloride crosslinking monomers (TAMAC) with dimethyldiallylammonium chloride(DMDAAC) (Scheme 1) [19]. Thus, in this article, the dye-fixing performances of these polycationic dye-fixatives on cotton



Scheme 1. Synthesis of slightly cross-linked PDMDAACs*

fabric [17, 18] were studied, and the roles of their intrinsic viscosities and molar content of TAMAC units in that performance were also examined in detail.

2. EXPERIMENTAL

2.1. *Materials*

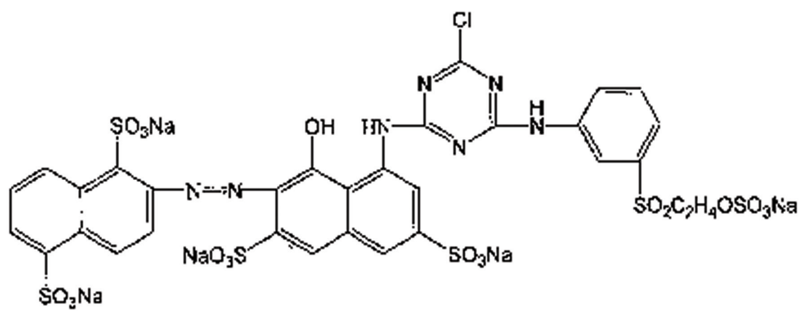
A series of slightly cross-linked PDMDAACs with controlled 1–5% molar ratios of crosslinking TAMAC and controlled intrinsic viscosities of 0.04–0.86 dl/g were synthesized by copolymerizing triallylmethylammonium chloride crosslinking monomers (TAMAC) with dimethyldiallylammonium chloride (DMDAAC), varying the molar ratio of TAMAC to DMDAAC from 1/99 to 5/95 and increasing the initial monomer concentration from 29% to 50% while decreasing the amount of initiator (ammonium persulphate, APS) from 19% to 5% during polymerization as described in our previous paper [19]. PDMDAAC with controlled molecular weights represented by an intrinsic viscosity of 0.41 dl/g were synthesized by homo-polymerization of dimethylammonium chloride at 60 ºC for 6 h and then ripening at 70 ºC for 2 h with an initial monomer concentration (*w*/*w*) of 52.5% and 3% initiator (*w*/*w*) according to our other previous contribution [16]. Reactive Scarlet 3BS and Brilliant Blue KNR were obtained from Jiangsu Nantong Chemicals and Textile Co., Ltd (China). Dye-fixative LYPF [42% (*w*/*w*) water solution, PDMDAAC dye-fixative] was purchased from Shangdong Luyue Chemical Co., Ltd, (China). Dye-fixative PDAC [40% (*w*/*w*) water solution, PDMDAAC dye-fixative] was purchased from Jiangsu Feixiang Chemical Co., Ltd, (China). Dye-fixative Fix [47% (*w*/*w*) water solution, cationic dye-fixative] was purchased from BASF Chemical Co., Ltd (Germany).

2.2. *Dye-fixing performances of slightly cross-linked PDMDAACs*

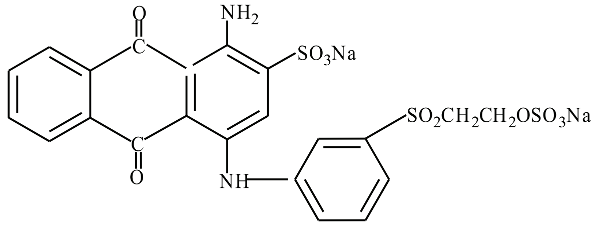
According to current widely-used dyeing and fixing processes (Scheme 2) [16], the cotton fabrics were dyed at 60 ºC with 2% (o.w.f) Reactive Scarlet 3BS (Scheme 3) or Brilliant Blue KNR (Scheme 4), which are both usually difficult to use for colouring cotton fabric. Then 3% (based on the weights of the fabrics, o.w.f) of each of the slightly cross-linked PDMDAACs were used to treat the dyed cotton fabrics at 60 ºC for 30 min. The pH of the fix application was 7 and the liquor ratio was 1:20 to investigate the dye-fixing performance of the slightly cross-linked PDMDAACs. In order to obtain an objective appraisal of the dye-fixing performance of the slightly cross-linked PDMDAACs, the values of the dyes' fastness on unfixed dyed-cotton samples (i.e., blank values) and the dye-fixing performances of a currently widely-used commercial polycationic PDMDAAC dye-fixative (Dye-fixative LYPF, Dye-fixative PDAC), a widely-used cationic Dye-fixative Fix, and selected PDMDAAC with an intrinsic viscosity of 0.41 dl/g, were also investigated under the same designed fixing conditions. The dye-fixing performances of all samples were evaluated by dry rubbing fastness, wet rubbing fastness, colour fastness to soaping, and white fabric staining.

Cotton fabric → Sodium sulfate and dyes, 45 min → Soda, 80 min → Washing with water → Washing with water → Washing with soap → Washing with water → Drying → Fixed by dye-fixatives

Scheme 2. Dyeing and fixing procedure on cotton fabric



Scheme 3. Structure of Reactive Scarlet 3BS



Scheme 4. Structure of Brilliant Blue KNR.

2.3. *Measurement*

The dry rubbing fastness and wet rubbing fastness represented by different colour fastness grades (i.e. grades 1–5), were measured using a rubbing fastness instrument (YB872, Dongguan Hongxing Instrument Factory) according to ISO 105-X12: 2001. Fixed cotton samples attached to white fabrics (4 cm × 10 cm) were washed in 50 ml soap solutions at 60 ºC for 30 min to test colour fastness to soaping and white fabric staining according to ISO 105-C10: 2006, both of which were represented by different colour fastness grades (i.e. grades 1–5).

3. RESULTS AND DISCUSSION

3.1. *Dye-fixing performances of slightly cross-linked PDMDAACs*

The slightly cross-linked PDMDAACs with various intrinsic viscosities obtained were further used to treat cotton fabrics dyed with Reactive Scarlet 3BS and Reactive Brilliant Blue KNR as described in Section 2.2, to investigate their dye-fixing performances. The results are given in Table 1.

The results showed their dye-fixing performances varied with their different intrinsic viscosities and molar ratios of crosslinking TAMAC units.

3.2. *Effect of intrinsic viscosities on dye-fixing performances*

Table 1 shows that at the same molar ratio of cross-linking TAMAC units in the main chains, the dye-fixing performances of slightly cross-linked PDMDAACs varied according to their different intrinsic viscosities. For example, the dye-fixing performances of Samples 1–9, with the same 1% molar ratio of TAMAC, varied with regard to their different intrinsic viscosities. Among them Samples 2–5, with intrinsic viscosities of 0.16–0.30 dl/g, exhibited better dye-fixing performances; in particular their wet rubbing fastness performances were 0.5 grades better than those of Samples 6–9, with intrinsic viscosities of 0.33–0.52 dl/g, and 1 grade better than that of Sample 1, with an intrinsic viscosity of 0.11 dl/g. This might be due to some possessing intrinsic viscosities too low, which would make the interactions of Van der Waals forces between slightly cross-linked PDMDAACs and dyes weak, resulting in poor dye-fixing performances. Conversely, if the intrinsic viscosities is too high it would make it difficult for them to penetrate into the cotton fabrics to interact with the dyes, also resulting in poor dye-fixing performances [16].

Keeping the above-mentioned general considerations regarding the effect of intrinsic viscosities on dye-fixing performances, those slightly cross-linked PDMDAACs possessing intrinsic viscosities in the 0.16–0.52 dl/g range stably exhibited better dye-fixing performances; among them, those with intrinsic viscosities of 0.16–0.30 dl/g exhibited the best dye-fixing performances.

3.3. *Effect of structure on dye-fixing performances*

Theoretically, the crosslinking plane-like structures in the slightly cross-linked PDMDAACs obtained should expand its interactions with dyes, possibly resulting in the development of improved dye-fixing performances (Scheme 5).

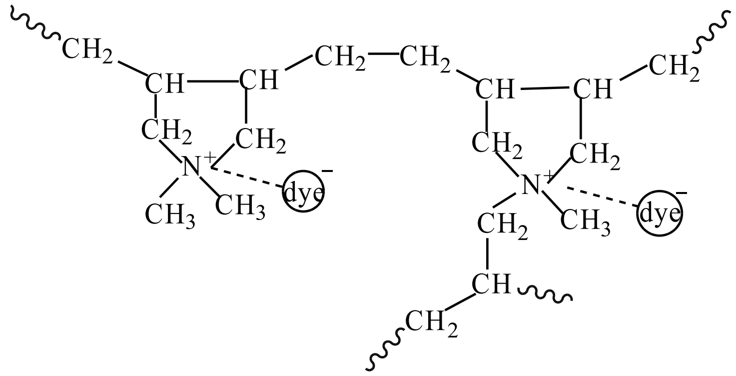
Moreover, Table 1 also shows that with similar intrinsic viscosities, the dye-fixing performances of slightly cross-linked PDMDAACs varied according to their different molar ratios of TAMAC units; for example, the dye-fixing performances of Samples 4, 19 and 29, with similar intrinsic viscosities of 0.24–0.27 dl/g, varied with respect to their different molar ratios of TAMAC; among them, Sample 4 with 1% TAMAC exhibited a better dye-fixing performance; in particular its wet rubbing fastness was 0.5 grades better than those of other samples

Table 1

Dye-fixing performances of slightly cross-linked PDMDAACs

Sample*	$n_{(TAMAC)}/n_{(DMDAAC)}$	Intrinsic viscosity (dl/g)	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	1/99	0.11	4	3	4–5	4–5	4–5	3	4–5	4–5
2	1/99	0.16	4	4	4–5	4–5	4–5	4	4–5	4–5
3	1/99	0.21	4	4	4–5	4–5	4–5	4	4–5	4–5
4	1/99	0.24	4	4	4–5	4–5	4–5	4	4–5	4–5
5	1/99	0.30	4	4	4–5	4–5	4–5	4	4–5	4–5
6	1/99	0.33	4	3–4	4–5	4–5	4–5	3–4	4–5	4–5
7	1/99	0.43	4	3–4	4–5	4–5	4–5	3–4	4–5	4–5
8	1/99	0.460	4	3–4	4–5	4–5	4–5	3–4	4–5	4–5
9	1/99	0.520	4	3–4	4–5	4–5	4–5	3–4	4–5	4–5
10	2/98	0.08	3–4	3	4–5	4–5	4–5	3	4–5	4–5
11	2/98	0.15	4	3	4–5	4–5	4–5	3–4	4–5	4–5
12	2/98	0.20	4	3–4	4–5	4–5	4–5	3–4	4–5	4–5
13	2/98	0.29	4	3–4	4–5	4–5	4–5	3–4	4–5	4–5
14	2/98	0.35	4	3–4	4–5	4–5	4–5	3–4	4–5	4–5
15	2/98	0.53	4	3	4–5	4–5	4–5	3–4	4–5	4–5
16	3/97	0.07	4	3	4–5	4–5	4–5	3	4–5	4–5
17	3/97	0.14	4	3	4–5	4–5	4–5	3–4	4–5	4–5
18	3/97	0.22	4	3–4	4–5	4–5	4–5	3–4	4–5	4–5
19	3/97	0.26	4	3–4	4–5	4–5	4–5	3–4	4–5	4–5
20	3/97	0.34	4	3–4	4–5	4–5	4–5	3–4	4–5	4–5
21	3/97	0.41	4	3–4	4–5	4–5	4–5	3–4	4–5	4–5
22	3/97	0.47	4	3	4–5	4–5	4–5	3–4	4–5	4–5
23	3/97	0.52	4	3	4–5	4–5	4–5	3–4	4–5	4–5
24	3/97	0.86	4	3	4–5	4–5	4–5	3–4	4–5	4–5
25	5/95	0.04	4	3	4–5	4–5	4–5	3	4–5	4–5
26	5/95	0.10	4	3	4–5	4–5	4–5	3–4	4–5	4–5
27	5/95	0.13	4	3	4–5	4–5	4–5	3–4	4–5	4–5
28	5/95	0.18	4	3–4	4–5	4–5	4–5	3–4	4–5	4–5
29	5/95	0.27	4	3–4	4–5	4–5	4–5	3–4	4–5	4–5
30	5/95	0.34	4	3–4	4–5	4–5	4–5	3–4	4–5	4–5
31	5/95	0.43	4	3	4–5	4–5	4–5	3–4	4–5	4–5
32	5/95	0.65	4	3	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 on all the samples was described in Section 2.1.



Scheme 5. The fixing interactions of slightly cross-linked PDMDAACs and anionic dyes

(19 and 29). Moreover, considering this general effect of structure on dye-fixing performances, the dye-fixing performances of slightly cross-linked PDMDAACs tended to decrease with increasing molar ratio of TAMAC from 1% to 5%. This might be due to their possessing too low a degree of cross-linking (derived from low molar ratios of TAMAC), making their interactions with dyes weak and resulting in poor dye-fixing performance. However, too high a degree of crosslinking (resulting from a high molar ratio of TAMAC) would make it more difficult for the dye-fixatives to penetrate into the cotton fabrics to interact with the dyes, due to their higher steric hindrance [17, 18].

3.4. *Combined effect of intrinsic viscosities and structures on dye-fixing performances*

Generally, the results in Table 1 showed, those slightly cross-linked PDMDAACs with intrinsic viscosities of 0.16–0.30 dl/g and 1% TAMAC tended to exhibit the best dye-fixing performances, due to the nice balance between their structures and intrinsic viscosities.

Compared to blank values, the dye-fixing performances of slightly cross-linked PDMDAACs with 0.16–0.30 dl/g and 1% TAMAC were improved 0.5–1 grades. In particular, the best wet rubbing fastness performance among these dye-fixatives was 1 grade better than those of commercial PDMDAAC dye-fixatives of LYPF and PDAC, and 0.5 grades better than that of commercial polycationic Dye-fixatives of Fix.

Moreover, the dye-fixing performances of slightly cross-linked PDMDAACs with 0.16–0.30 dl/g and 1% TAMAC were better than those of the selected molecular-weight-controlled PDMDAAC, indicating that the performances of those PDMDAAC-based dye-fixatives could be further developed by incorporation of 1% TAMAC into the main chains of molecular-weight-controlled poly(dimethyldiallylammonium chloride) (PDMDAAC) dye-fixatives.

It could be summarized from above-mentioned results that those slightly cross-linked PDMDAACs with 0.16–0.30 dl/g and 1% TAMAC could be expected to fine use as novel dye-fixatives on cotton fabric.

In addition, the colour fastness (especially the wet rubbing fastness) of Reactive Brilliant Blue KNR fixed by slightly cross-linked PDMDAACs with intrinsic viscosities of 0.16–0.30 dl/g and 1% molar TAMAC appeared to be slightly better than that of Reactive Scarlet 3BS under the same fixing conditions, because there was a lower content (just two) of sulfonate anions in the structure of Reactive Brilliant Blue KNR than that of Reactive Scarlet 3BS, possibly resulting in a higher water resistance of the colour lakes derived from interactions of Reactive Brilliant Blue KNR with the slightly cross-linked PDMDAACs during fixing. Moreover, the amine groups of Reactive Brilliant Blue KNR could bring about more effective hydrogen bonds with the hydroxyl groups of cotton (cellulose), also possibly resulting in higher colour fastness.

4. CONCLUSIONS

(1) Dye-fixing performances were affected by the molar content of crosslinking TAMAC units in the main chains as well as their intrinsic viscosities.

(2) Those slightly cross-linked PDMDAACs with intrinsic viscosities of 0.16–0.30 dl/g and a 1% molar TAMAC tended to exhibit the best dye-fixing performances, due to the nice balance between their structures and intrinsic viscosities; their performances were better than any of the widely-used commercial polycationic dye-fixatives delected; they can expect to find use as novel dye-fixatives on cotton fabric. Moreover, it appears that the dye-fixing performances of these PDMDAAC-based dye-fixatives could be further developed by incorporation of 1% TAMAC in molecular-weight-controlled poly(dimethyldiallylammonium chloride) dye-fixatives.

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