

Synthesis and Application of Block Copolymeric Formaldehyde Scavenger

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Abstract: The amphipathic block copolymers used as formaldehyde scavenger were successfully prepared with the microemulsion polymerization method. The chemical reaction used hydrophilic monomer X with acylamide groups and hydrophobic monomer Y as reactants, potassium persulfate as initiator, dodecyl sodium sulfate as emulsifier, and the amphipathic block copolymers were produced after Hofmann degradation. Products made under different reaction conditions were applied in the rabbit skin tanned with formaldehyde and the amount of free formaldehyde left was detected. By range analysis and variance analysis of the orthogonal experimental results, the best synthetic condition was optimized as follow: the mole ratio of X and Y was 16.5:1, the mole percent of initiator was 0.9%, the mole ratio of X, NaClO and NaOH was 1:1:1.25, reaction time was 2h and reaction temperature was 90°C. The optimal product could reduce free formaldehyde by 30%. Also, the physical and mechanical properties of the rabbit skin and the dyeing effect were improved, which showed that the product had additional retanning and auxiliary dyeing property. The structure of the product was characterized by FT-IR, H-NMR and DSC, the results indicated that the amphipathic block copolymers had been successfully obtained and parts of the acylamide groups had converted into amino groups via Hofmann degradation.

Key words: formaldehyde scavenger; block copolymer; retanning property; auxiliary dyeing property

1 Introduction

Formaldehyde is used in the fields of disinfection, sterilization, antiseptis, organic synthesis and so on. As an ancient tanning method, formaldehyde tanning has the advantage of low cost, easy operation and simple control. In the tanning process, formaldehyde mainly combines with the amino and imino groups on the collagen fibers, but the reaction is reversible, so free formaldehyde could be released after a period of time. For being cancerigenic, formaldehyde content has been strictly limited in leather and fur product^[1]. However, formaldehyde tanning hasn't been completely abandoned in some fur making process, for the reason that furs tanned by formaldehyde have an outstanding fastness to water, perspiration, solvent, alkali, oxidation and reduction. Furthermore, most of the resin and synthetic tanning agents which have been used considerably in leather making are produced via a process of condensation polymerization with formaldehyde. These chemicals could also bring free formaldehyde to leather or fur products. Therefore, it is necessary to study on how to decrease the amount of free formaldehyde in leather and fur products.

The method to produce amphipathic block copolymers includes controllable/active radical polymerization^[2-5], ion ring-opening polymerization^[6], active anionic polymerization^[6], RAFT^[7], cationic polymerization^[8]. In this paper, the amphipathic block copolymers were prepared by microemulsion polymerization method and Hofmann degradation, using hydrophilic monomer X with acylamide groups and hydrophobic monomer Y as reactants, potassium persulfate as initiator, dodecyl sodium sulfate as emulsifier. The block copolymeric structure and amino groups were expected to help

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capture the free formaldehyde molecules, as well as to give the fur a retanning and auxiliary dyeing effect.

2 Experimental

2.1 Materials

In this paper, chemicals used for synthesis and analysis were analytical reagents.

2.2 Preparation method

2.2.1 Preparation of amphipathic block copolymers

Dissolve certain amount of sodium lauryl into the solution of hydrophilic monomer X, and then add hydrophobic monomer Y, the whole would form into a transparent microemulsion. Pour the microemulsion into a three-neck flask installed with a stirrer and a reflux condenser. Under the set temperature, add potassium persulfate and keep the reaction for the period of time required. Then stop the reaction using an icewater bath, and add the mixed solution of NaClO and NaOH, allowing the Hofmann degradation last for 2h. To improve the percent conversion, continue the reaction inside an icebox for over 12h.

To prepare for the following tests, adjust the pH of the product to 8.

2.2.2 Orthogonal test

The preparation conditions were optimized by a series of orthogonal tests. According to the factors and levels required to be examined, orthogonal array $L_{27}(3^{13})$ was selected. See Table 1.

Tab. 1 Factors and levels of orthogonal tests

A	B	C	D
Mole ratio of X and Y	Mole percent of initiator (%)	Mole ratio of X and NaClO	Mole ratio of X and NaOH
16.5:1	0.8	1:0.9	1:2.5
17:1	0.9	1:1	1:3
17.5:1	1.0	1:1.1	1:3.5

2.3 Performance test

Prepare formaldehyde tanned rabbit furskins for the following tests.

2.3.1 Free formaldehyde capturing test

Divide the skins along backbone and note down the weight, one half for the capturing test, the other half for the blank test.

After wetback, the skin was mixed with water ten times the dried skin weight and 5g/L of the prepared product. Oscillate for 2h under normal temperature, and then determine the formaldehyde content in the bath [9]. Blank test was performed following the same process only no scavenger added.

The skins were used for the following retanning and dyeing tests.

2.3.2 Retanning and dyeing test

The skins were retanned and dyed based on the recipes in Table 2. The dyestuffs used in the tests included acid dye, direct dye and metal complex dye. The residual dye bath was used to determine the absorbance value and K/S value, and the crusts were used to measure the physical and mechanical properties^[10-15].

The formula for calculating the rate of dye uptake is:

$$\text{Uptake (\%)} = (1 - E_1/E_0) \times 100$$

Where: E_0 = absorbance value of the fresh dye liquor

E_1 = absorbance value of the residual dye bath

Tab. 2 Retanning and dyeing process

Process	Materials	Amount(g/L)	Time (min.)	Temperature(°C)	Remarks
Chrometan	H ₂ O	20:1	15		
	HCOOH	1			
	Chrome powder	10	90	38	
	Fatliquor RAN	3	30		
	HCOONa	2	30		
Neutralizæ	NaHCO ₃	x	90		pH: 3.8 Drain
	H ₂ O	20:1		38	
	PAN-K	2	30		
	HCOONa	2	30		
Dye	NaHCO ₃	1	90		Check. Drain
	H ₂ O	20:1		65	
	Levelling agent FF	1			
	Ammonia (25%)	1	20		
	Fatliquor RAN	2	30		
	Dyestuff	2	90		Check Ø
	Fatliquor	2	60		
Wash hair	HCOOH	1.5	2 × 30		pH=3.5 Drain. Wash
	H ₂ O	20:1		40	
	Washing hair agent FL-80	0.5	30		
	HCOOH	0.3	30		

2.4 Structure characterization of the amphipathic block copolymer

The block copolymer was precipitated with methanol, after many repetitions, then immersed in toluene for 48h to remove the polystyrene homopolymers. The residue was dried and prepared for FT-IR, H-NMR and DSC analysis.

3 Results and discussion

3.1 Results of orthogonal test

Results are shown in Table 3, 4 and 5.

From range analysis in Table 4, influence order of the factors and interactions is: $A > (A \times C)_2 > C > (A \times B)_1 > D > B > (A \times C)_1 > (A \times B)_2$. So the greatest influence on capture rate is the mole ratio of hydrophilic X and hydrophobic Y (Factor A), followed by Interaction $A \times C$, which stands for mole ratio of X, Y and NaClO. Variance analyses in Table 5 also show their degree of influence is of significance or secondary significance.

If not considering the interactions, the best combination of the factors is $A_1B_2C_3D_1$. As the interaction between A and C has some important influence, they were singled out for dichotomic analysis. See Table 6. Capture rate is a larger-the-better index and hence A_1C_2 is selected.

In summary, the best preparation condition is $A_1B_2C_2D_1$. Prepare the optimized product in accordance with the data of $A_1B_2C_2D_1$. The product was a transparent light brown liquid. Capturing test showed that the capture rate achieved to 30%.

Tab. 3 Design and results of orthogonal test

No.	1 A	2 B	3 A×B	4 A×B	5	6	7	8 C	9 A×C	10 A×C	11	12 D	13	Capture rate (%)
1	1	1	1	1	1	1	1	1	1	1	1	1	1	33.3
2	1	1	1	1	2	2	2	2	2	2	2	2	2	25.6
3	1	1	1	1	3	3	3	3	3	3	3	3	3	23.4
4	1	2	2	2	1	1	1	2	2	2	3	3	3	29.7
5	1	2	2	2	2	2	2	3	3	3	1	1	1	28.8
6	1	2	2	2	3	3	3	1	1	1	2	2	2	25.9
7	1	3	3	3	1	1	1	3	3	3	2	2	2	26.0
8	1	3	3	3	2	2	2	1	1	1	3	3	3	19.2
9	1	3	3	3	3	3	3	2	2	2	1	1	1	37.4
10	2	1	2	3	1	2	3	1	2	3	1	2	3	5.9
11	2	1	2	3	2	3	1	2	3	1	2	3	1	16.8
12	2	1	2	3	3	1	2	3	1	2	3	1	2	4.7
13	2	2	3	1	1	2	3	2	3	1	3	1	2	16.3
14	2	2	3	1	2	3	1	3	1	2	1	2	3	30.4
15	2	2	3	1	3	1	2	1	2	3	2	3	1	2.5
16	2	3	1	2	1	2	3	3	1	2	2	3	1	21
17	2	3	1	2	2	3	1	1	2	3	3	1	2	7.4
18	2	3	1	2	3	1	2	2	3	1	1	2	3	16.4
19	3	1	3	2	1	3	2	1	3	2	1	3	2	17.6
20	3	1	3	2	2	1	3	2	1	3	2	1	3	15.3
21	3	1	3	2	3	2	1	3	2	1	3	2	1	12.7
22	3	2	1	3	1	3	2	2	1	3	3	2	1	0
23	3	2	1	3	2	1	3	3	2	1	1	3	2	25.1
24	3	2	1	3	3	2	1	1	3	2	2	1	3	23.1
25	3	3	2	1	1	3	2	3	2	1	2	1	3	15.6
26	3	3	2	1	2	1	3	1	3	2	3	2	1	12.1
27	3	3	2	1	3	2	1	2	1	3	1	3	2	10.1

Tab. 4 Results of range analysis

Factor	A	B	A×B	A×B	Empty column			C	A×C	A×C	Empty column	D	Empty column
	1	2	3	4	5	6	7	8	9	10	11	12	13
AVG ₁	27.7	17.3	19.5	18.8	18.4	18.3	21.0	16.3	17.8	20.1	22.8	20.2	18.3
AVG ₂	13.5	20.2	16.6	19.4	20.1	18.1	14.5	18.6	18.0	22.4	19.1	17.2	17.6
AVG ₃	14.6	18.3	19.7	17.6	17.4	19.4	20.3	20.8	20.0	13.3	13.9	18.4	19.9
Range	14.2	2.9	3.1	1.8	2.7	1.3	6.5	4.5	2.2	9.1	8.9	3.0	2.3
k _{1j}	249.3	155.3	175.2	169.2	165.4	165.1	189.4	147	159.9	181.2	204.9	181.8	164.6
k _{2j}	121.3	181.6	149.5	174.7	180.5	162.6	130.3	167.6	161.8	201.5	171.8	155.0	158.6
k _{3j}	131.5	165.2	177.3	158.2	156.2	174.4	182.3	187.5	180.4	119.4	125.3	165.3	178.9
k ₁ ^{2j}	6.2×10 ⁴	2.4×10 ⁴	3.1×10 ⁴	2.9×10 ⁴	2.7×10 ⁴	2.7×10 ⁴	3.6×10 ⁴	2.2×10 ⁴	2.6×10 ⁴	3.3×10 ⁴	4.2×10 ⁴	3.3×10 ⁴	2.7×10 ⁴
k ₂ ^{2j}	1.5×10 ⁴	3.3×10 ⁴	2.2×10 ⁴	3.1×10 ⁴	3.3×10 ⁴	2.6×10 ⁴	1.7×10 ⁴	2.8×10 ⁴	2.6×10 ⁴	4.1×10 ⁴	3.0×10 ⁴	2.4×10 ⁴	2.5×10 ⁴
k ₃ ^{2j}	1.7×10 ⁴	2.7×10 ⁴	3.1×10 ⁴	2.5×10 ⁴	2.4×10 ⁴	3.0×10 ⁴	3.3×10 ⁴	3.5×10 ⁴	3.2×10 ⁴	1.4×10 ⁴	1.6×10 ⁴	2.7×10 ⁴	3.2×10 ⁴
Order	A > (A × C) ₂ > C > (A × B) ₁ > D > B > (A × C) ₁ > (A × B) ₂												

Tab. 5 Results of variance analysis

Variance Source	Deviance	Freedom	Variance	F	Fa	Significance
A	1124.5	2	562.3	8.6	19.4	significant
B	39.1	2	19.6	0.3	99.4	insignificant
A×B	69.1	4	17.3	0.3	5.96	insignificant
C	91.3	2	45.6	0.7	14.55	insignificant
A×C	435.5	4	108.9	1.7	3.38	secondary
D	40.6	2	20.3	0.3	2.08	insignificant
Error	653.2	10	65.3			

Tab. 6 Results of interaction between Factor A and C

	A ₁	A ₂	A ₃
C ₁	26.1	5.3	17.6
C ₂	30.9	16.5	8.5
C ₃	26.1	18.7	17.8

3.2 Retanning property

Table 7 shows that when use the formaldehyde scavenger after tanning, rabbit skin had increase in all the physical and mechanical property indexes compared with the blank sample. Therefore, it demonstrates that the product had retanning property.

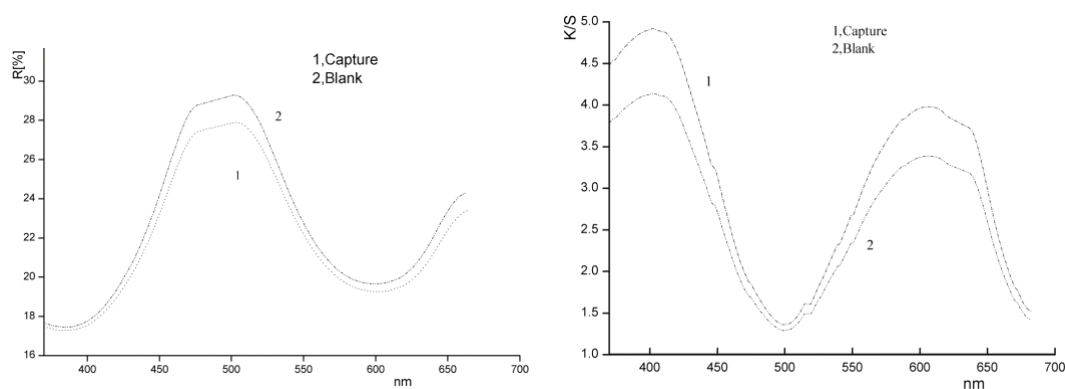
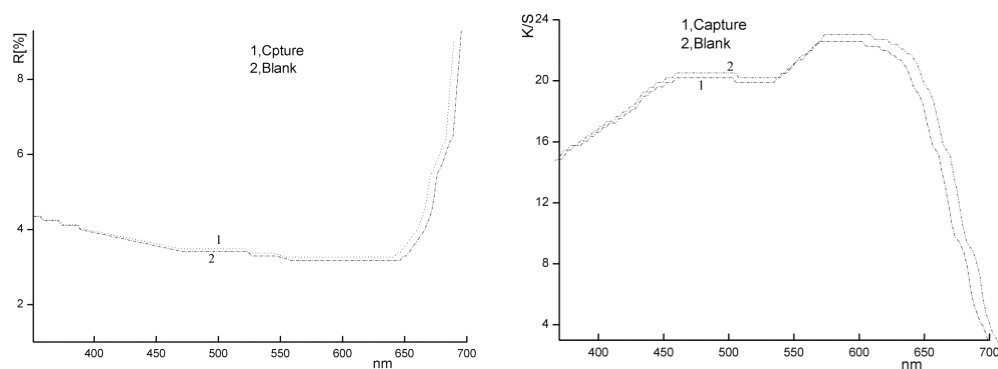
Tab. 7 Results of interaction between Factor A and C

Sample	Substance increase (%)	Ts(°C)	Tensile strength (N/mm ²)	Tear strength (N/mm)	Elongation at given load (%)	Elongation at break (%)
Blank		99.6	64	126	63	86
Capture	11	105.7	100	167	76	118

3.3 Auxiliary dyeing property

Tab. 8 Auxiliary effect on different dyestuffs

	Dye uptake (%)		Dry rub fastness		Wet rub fastness	
	Blank	Capture	Blank	Capture	Blank	Capture
Acid dye	58%	71%	3	4.5	3	4
Metal complex dye	63%	64%	2.5	2	2.5	2.5
Direct dye	63%	70%	2	2.5	2	3

**Fig. 1 Influence on dyeing property of acid dye****Fig. 2 Influence on dyeing property of metal complex dye**

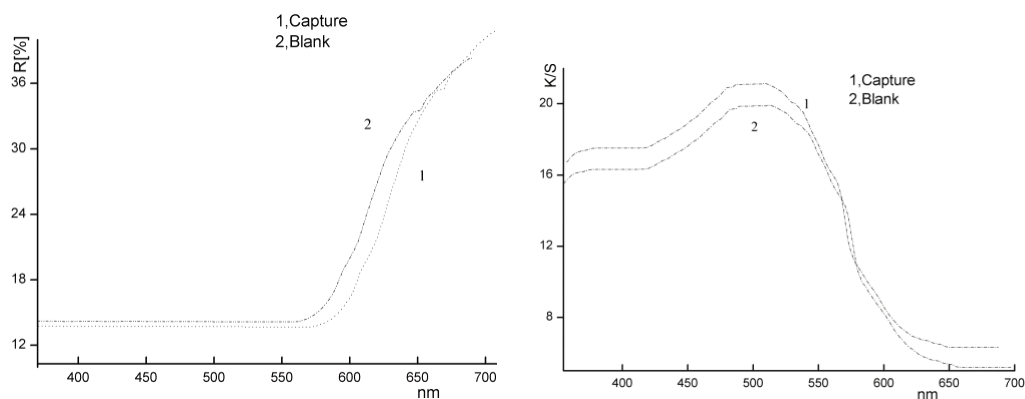


Fig. 3 Influence on dyeing property of direct dye

From Table 8, conclusions could be drawn as follows:

(1) To acid dye and direct dye, the product had favorable dyeing effect as the dye uptake and dry/wet rub fastness were both higher than blank sample. The K/S value in Fig. 1 and Fig. 3 also shows color of the capture sample was deeper.

(2) To metal complex dye, the product had no auxiliary effect as the dye uptake and dry/wet rub fastness showed little change compared with blank sample, which could also be seen from the K/S value in Fig. 2.

3.4 Results of structure characterization

3.4.1 Infrared spectrum analysis

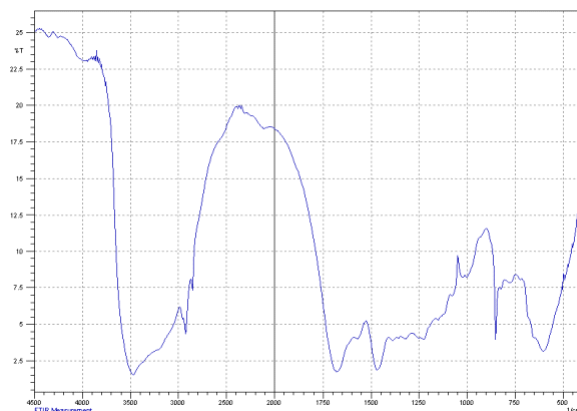


Fig. 4 FT-IR of the amphipathic block copolymer

From the FT-IR spectra in Fig. 4, analyses can be made as follows:

1470cm^{-1} is where the benzene ring makes the characteristic absorption, 850cm^{-1} is where the mono-substituted benzene ring makes the characteristic absorption 2945.45cm^{-1} stands for the asymmetric stretching vibration of $-\text{CH}_2-$, 2881.64cm^{-1} stands for the symmetrical stretching vibration of $-\text{CH}_2-$. Above are the characteristic absorptions of the hydrophobic groups.

3480cm^{-1} stands for the stretching vibration of N-H in primary amine, 1566.53cm^{-1} stands for the in-plane bending vibration of N-H, 1675cm^{-1} stands for the symmetrical stretching vibration of $\text{C}=\text{O}$. Above are the characteristic absorptions of the hydrophilic groups.

In conclusion, both hydrophobic and hydrophilic groups could be found in the product molecule, which demonstrate the copolymer was an amphipathic molecule.

3.4.2 $^1\text{H-NMR}$ analysis

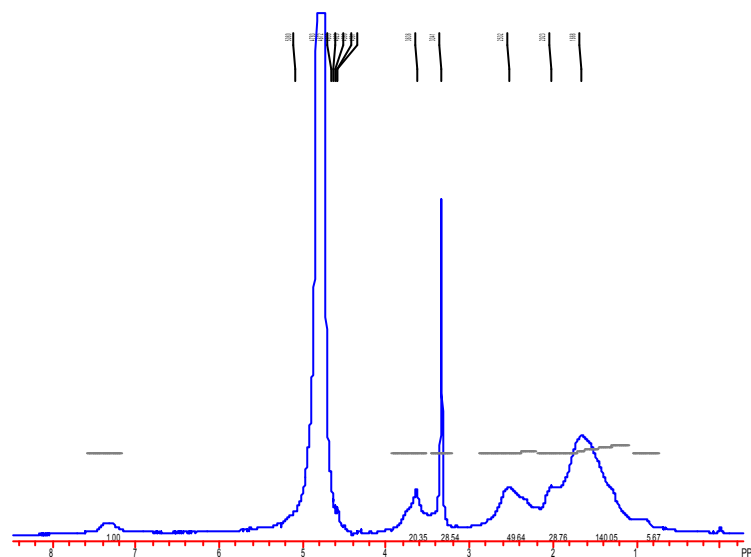


Fig. 5 H-NMR of the amphipathic block copolymer

From Fig. 5, it can be seen that spectral configurations have great difference between the monomers and copolymer. The strong peak at $\delta = 4.795$ is the proton signal of -NH_2 , which proves amino groups were produced via Hofmann degradation. Peak at $\delta = 2.182$ is considered to be the proton signal of methylene in hydrophobic group. Hence, amphipathic structure was further confirmed by H-NMR analysis.

3.4.3 DSC analysis

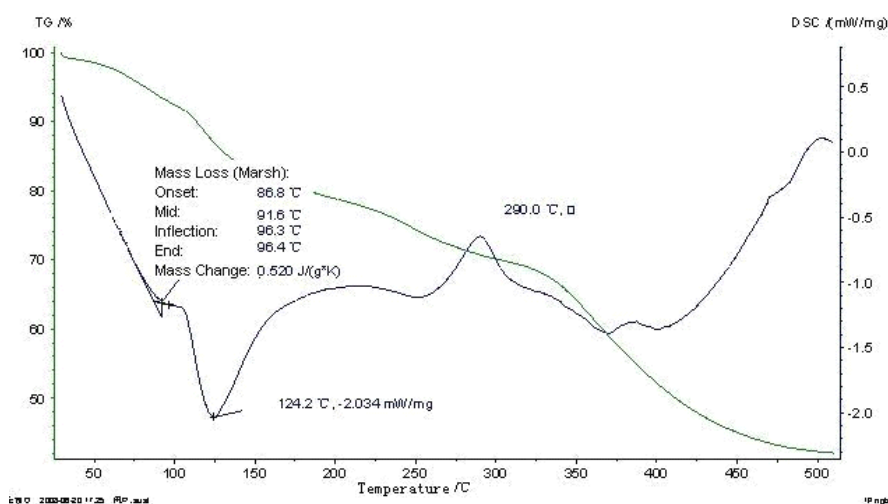


Fig. 6 DSC curve of the amphipathic block copolymer

The curve in Fig. 6 shows that at the point of 124°C, 370°C and 400°C, three endothermic peaks appear, which demonstrate the product had block copolymeric structure. With temperature rising from 0°C to 500°C, the mass loss came to 57.96%, indicating the product had certain degree of heat stability.

4 Conclusions

1) The optimal preparation condition was: the mole ratio of X and Y 16.5:1, the mole percent of initiator 0.9%, the mole ratio of X, NaClO and NaOH 1:1:1.25, reaction time 2h and reaction temperature 90°C.

2) The optimal product could reduce free formaldehyde by 30%. It also had additional retanning and auxiliary dyeing property. However, only for acid dye and direct dye did it show favorable dyeing effect, while for metal complex dye, no auxiliary effect had been demonstrated.

3) FT-IR and H-NMR analysis showed that hydrophilic and hydrophobic monomers have been successfully polymerized, and parts of the acylamide groups had converted into amino groups via Hofmann degradation. DSC analysis confirmed that block copolymeric structure had been formed.

References

- [1] F. X. Cheng; Y. X. Zhou; Q. P. Zhu. China Leather, 2006, 35(23): 33-38.
- [2] X. D. Tang; X. H. Fan; X. F. Chen. Chinese Polymer Bulletin, 2006, (6): 36-43.
- [3] J. Cao; K. D. Zhang; L. Wang. Polymer Materials Science and Engineering, 2005, 21(3): 81-44.
- [4] C. L. He; H. W. Yao. Journal of Qingdao University, 2007, 22(1): 54-57.
- [5] C. Y. Hong; C. Y. Pan. Chemistry Online, 2003, 33(12): 807-814.
- [6] C. Y. Hong; C. Y. Pan. Chemistry Online, 2004, (5): 317-326.
- [7] W. X. Chen; X. D. Fan; Y. Y. Liu; etc. Polymer Materials Science and Engineering, 2006, 22(3): 88-92.
- [8] R. F. Zhang; J. Lu. Chinese Polymer Bulletin, 2000, (3): 46-52.
- [9] F. X. Cheng; Y. X. Zhou; X. J. Zhu; etc. Free formaldehyde scavenger of leather and fur, The 7th Asian International Conference of Leather Science and Technology, 170-178.
- [10] QB/T1267-1991
- [11] QB/T1266-1991
- [12] QB/T1269-1991
- [13] QB/T1270-1991
- [14] QB/T1268-1991
- [15] QB/T1271-1991