

SYNTHESIS OF HYPERBRANCHED POLYMER WITH TERMINAL AMIDOGEN AND ITS APPLICATION AS FORMALDEHYDE SCAVENGER IN LEATHER

by

WANG XUECHUAN, REN LONGFANG*, QIANG TAOTAO

College of resource & environment, Shaanxi University of Science & Technology,
Xi'AN, SHAANXI, P.R. CHINA 710021

ABSTRACT

A hyperbranched polymer with terminal amidogen was synthesized with succinic anhydride and diethylenetriamine by "one-step method", and then it was characterized through FT-IR and GPC testing. Moreover, the prepared hyperbranched polymer with terminal amidogen was used to remove free formaldehyde in leather tanned by organic phosphonium tanning agent. The application results indicated that the formaldehyde de-removal percentage of hyperbranched polymer with terminal amidogen reached 60.4%. The formaldehyde content of leather reduced to less 50mg/kg. Comparing with other formaldehyde scavengers, its formaldehyde-removal effect was much better. The thickening rate and dye absorptivity of the polymer were 16.7% and 96.5% respectively, so it also had thickening and assisting dyeing effects to leather.

RESUMEN

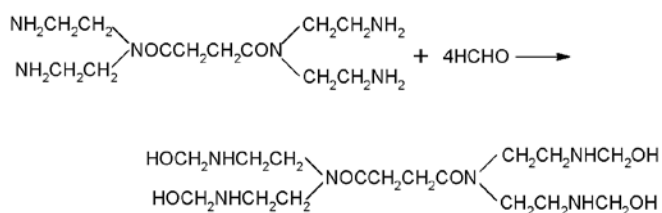
Un polímero hiper-ramificado con terminal amidógeno fue sintetizado con anhídrido succínico y dietilentriamina por "un método de un paso" y, a continuación, se caracterizó mediante pruebas de FT-IR y GPC. Por otra parte, el polímero hiper-ramificado preparado con terminal amidógeno fue utilizado para eliminar el formaldehído libre en el cuero curtido con fosfonio orgánico como agente curtiente. Los resultados indicaron que el porcentaje de remoción del formaldehído del polímero hiper-ramificado con terminal amidógeno alcanzó 60,4%. El contenido de formaldehído en el cuero fue reducido a menos 50mg/kg. Comparando con otros removedores de formaldehído, el efecto de eliminación del formaldehído fue mucho mejor. El grado de engrosamiento y la absorción de la tintura del polímero fueron 16,7% y 96,5% respectivamente, por lo que también hubo aumento de espesor y un efecto de asistencia al teñido en el cuero.

INTRODUCTION

As we all know, formaldehyde is classified as a suspected carcinogen.¹ In the case of a human being exposed to a low concentration of formaldehyde gas, the formaldehyde is pungent to the mucosa of the eye, nose, and respiratory tract and acts as a lachrymator causing sneezing and coughing.² Because many chemical materials are used in leather manufacturing process, some hazardous substances are left in leather.³ Formaldehyde is one of hazardous substances, so its content in leather must be lower than limited values. The DIN standard for maximum tolerance limit for formaldehyde in finished leather articles for adults is 150ppm and for children is 75ppm.⁴ Formaldehyde is a kind of cross-linking agent with excellent properties and there is no new substitute until now, so researching and developing formaldehyde scavenger with good performances is imperative under the situation.⁵ Researchers have paid more attention to the study on formaldehyde scavenger. At present, amino derivatives,^{6,7} porous inorganic fillers,^{8,9} strong oxidative materials¹⁰ and compounds with α -hydrogen^{11,12} are the main formaldehyde scavenger.

Because hyperbranched polymer has high reactivity, low viscosity, good solubility, and special branched structure, it is used in many fields; however, the application in leather is minimal. The molecular shape of hyperbranched polymer is similar to spherical and there are large numbers of active groups around molecule. If the end-groups of hyperbranched polymer are amidogen, they can react with formaldehyde, so that it can be used as formaldehyde scavenger. The reaction formula is shown in scheme 1. The studies on application of hyperbranched polymer with terminal amidogen in other fields are common,¹³⁻¹⁶ but nobody researched their application in leather industry. In the paper, a hyperbranched polymer with terminal amidogen is synthesized with succinic anhydride and diethylenetriamine by "one-step method". It is used to remove free formaldehyde in leather and the applying effect is studied.

* Corresponding Author - e-mail address: renlf1010@163.com, Fax: 86-02986168291
Manuscript received December 28, 2007, accepted for publication May 19, 2008



Scheme 1: The reactive schematic plots of hyperbranched polymer with terminal amidogen and formaldehyde

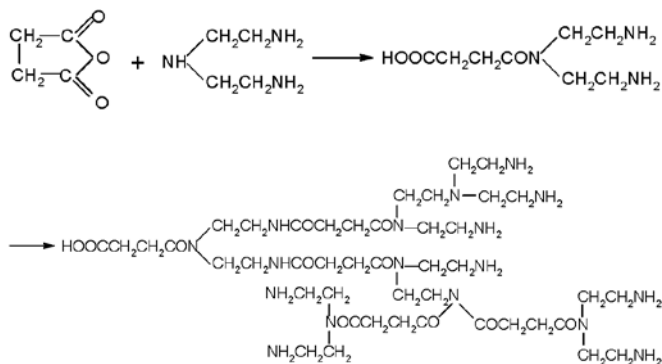
EXPERIMENTAL

Materials and apparatus

Succinic anhydride, diethylenetriamine and chloroform (AR) were provided by Ke Mi-ou chemical reagent factory in Tianjin. Sodium hyposulfite and iodine were supplied by Hua Bo-zhan chemical factory in Xi'an. Granofin FCC was organic phosphonium tanning agent and offered by Clariant Company. Other materials used in procedure also were supplied by Clariant Company. Pickled goatskins were provided by Yantai leather manufacturing Company in Shandong. W2-180SP rotary evaporator was supplied by Shensheng Science and Technology Ltd. Company; G02515911M515 gel permeation chromatography(GPC) was provided by Waters Company of USA; VECTOR-22 Fourier Transform Infrared(FT-IR) spectrometer was offered by Bruke Company of Germany.

Synthesis of hyperbranched polymer with terminal amidogen¹⁷

50g diethylenetriamine was weighed and placed in three-neck flask. 48.5g succinic anhydride was dissolved in chloroform and compound solution was slowly dripped into the flask. The reaction was kept for 0.5h. Chloroform in above reaction product was removed in rotary evaporator, and then the reaction was kept for 4h in vacuum under 150°C. The light yellow hyperbranched polymer with terminal amidogen was obtained. The reaction formula was as follows:



Scheme 2: The reactive schematic plots of hyperbranched polymer with terminal amido

The characterization of hyperbranched polymer with terminal amidogen

FT-IR testing: The diethylenetriamine and hyperbranched polymer with terminal amidogen were dried at 105°C for 24h, and then tested by coating method; the succinic anhydride was mixed with potassium bromide and pressed into pellets under reduced pressure. The FT-IR spectra were obtained by scanning.

GPC testing: The hyperbranched polymer with terminal amidogen was diluted to a concentration of approximately 2mg/mL. The solution was injected from the top of chromatogram column. The polyethylene glycol was as reference and the analysis was carried out using GPC apparatus.

The applying procedure of hyperbranched polymer with terminal amidogen

The reaction of amidogen and aldehyde group contained two steps which were nucleophilic addition and β -hydride elimination reaction. Firstly, the lone electron pair in amidogen attacked aldehyde group. Secondly, proton transfer happened quickly. Finally, the stable enamine was formed by dehydration. The reaction was greatly influenced by pH. In strong acid medium the amidogen was protonized, there was not lone electron pair to bombard aldehyde group, as a result, the reaction was restrained. But if an even more alkaline medium was used, alkali would combine with a proton and influence the transfer and dehydration of proton. For this reason it was favorable to use hyperbranched polymer with terminal amidogen between neutralization and fixing procedure with formic acid during organic phosphonium tanning process. Moreover, it was compared with other formaldehyde-removal agent. For other formaldehyde scavengers, the reaction mechanism of 1, 6-hexanediamine, urea and formaldehyde were the same as that of hyperbranched polymer with terminal amidogen. For hydrogen peroxide and sodium bisulfite, the effect of pH on their reaction with formaldehyde was minimal, so they all could be used in the part of the formula. The tanning procedure was shown in TABLE I.

Determination of free-formaldehyde content

Extraction: The leather tanned by organic phosphonium tanning agent was dried and cut into small pieces. 2.0g small leather pieces and 50mL water were placed in 250mL iodine flask immersed in a 40°C water bath for 3h.¹⁸ The formaldehyde in the aqueous phase was then detected by conventional techniques. The extracted leather was dried in oven and its weight was the base of calculating formaldehyde content in leather.

TABLE I
The tanning procedure of organic phosphonium tanning agent

Process	%	Chemicals	T	Min.	pH	Comments
Depickling/Taning	80	Water	20			
	8.0	Salt		5		
		Skins		20	3.4	
	1.0	Sodium Formate		60	3.6	
	2.0	Granofin FCC		120		Check Over night
	1.0	Feliderm DP				
	1.0	Catalix L		60		
	1.6	Sodium Bicarbonate		5X30+60	5.7	
	2.0	Tanicor CRF		60		
WASH	150	Water	20			
	0.6	Sodium Perborate		60		check
HORSE						
Shave 0.55-0.6mm						
WASH	300	Water	40			
	1.5	Tergolix SL-01				
	0.3	Oxalic acid				
	0.2	Feliderm MPP		60	5.4	
WASH	300	Water	45			
	0.5	Oxalic acid				
	0.4	Tergolix SL-01				
	0.2	Feliderm MPP		60	5.4	
DRIAN						
WASH	300	Water	35	10		
	DRAIN					
RETAN						
WASH	100	Water	35			
	4.0	Derminol RA				
	3.0	Derminol NLM				
	4.0	Tergotan TSP		60		
	6.0	Tanicor SCU				
	4.0	Granifin TA		60		
	100	Water	45	5		
	3.0	Derminol RA				
	3.0	Derminol SF				
	3.0	Derminol ALE		60		
	3.0	Formaldehyde scavenger		60		
	2.0	Black dye		60		
	0.5	Formic acid		10		
	1.0	Formic acid		45	3.5	
	1.5	Dermagen PC		30	3.8	
	WASH	300	water	20	10	
FATLIQUOR						
WASH	150	Water	45			
	3.0	Catalix L				
	3.0	Catalix U				
	3.0	Dermafinish LB		60		
	1.0	Formic acid		30	3.5	
	1.0	Derminol SF		20		
	1.0	Demagen PC		30	3.8	
	0.5	Formic acid		20	3.4	WASH/HORSE

Determination of free-formaldehyde:¹⁹ 5mL above filtrate was added into 50mL iodine flask, and then 25mL iodine standard solution and 15mL sodium hydroxide whose concentration was 1mol/L were put into flask. After 15min, 40mL sulfuric acid whose concentration was 1mol/L was added into iodine flask. The above solution was titrated with 0.1mol/L sodium hyposulfite. When solution was light yellow, 1mL starch indicator was added, and then titration was carried out until blue disappeared. The calculating formula was as follows:

$$\text{Formaldehyde content}/\% = \frac{(C_1V_1 - C_2V_2) \times 15.02 \times 10^{-3}}{M} \times 100\% \quad (1)$$

Where C_1 and C_2 were the concentration of iodine standard solution and concentration of sodium hyposulfite standard solution (mol/L); V_1 and V_2 respectively represented volume of iodine standard solution and wasting volume of sodium hyposulfite standard solution (mL); M was weight of leather (g); 15.02 represented molar mass of formaldehyde (g/mol).

$$\text{Formaldehyde-removal percentage}/\% = \frac{W_1 - W_2}{W_1} \times 100\% \quad (2)$$

In the formula, W_1 was formaldehyde content in blank sample and W_2 was formaldehyde content in leather treated with formaldehyde scavenger (mg/kg).

RESULTS AND DISCUSSION

FT-IR analysis

As is known, FTIR was used to determine characteristics of a compound which depend on its functional groups appearing in the FT-IR fingerprint region. As pointed out by Nakagawa and Sugita it was believed that characterization of vegetable tannins by spectroscopy stands a good chance of success and in the study results they carried out.^{20,21} So characteristic absorption patterns would make it possible for us to characterize the structure of product. The FT-IR spectra of reactants and product were shown in Figure 1, 2, 3, respectively.

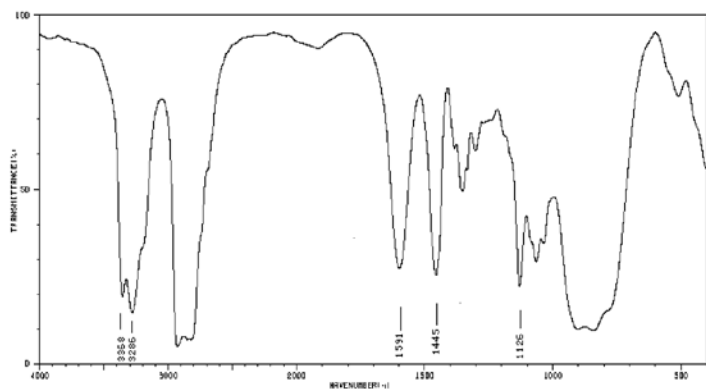


Figure 1: FT-IR spectrum of diethylenetriamine

As shown in Figure 1, 3368 cm^{-1} and 3286 cm^{-1} were the stretching vibration peak of N-H in amidogen, but in Figure 3 it became the overlapped peak of N-H bond in amide groups and amidogen in 3358 cm^{-1} . There was C-N bond of 1445 cm^{-1} in Figure 1, but it disappeared in Figure 3. In Figure 2 the stretching vibration coupling peak of C=O bond in alicyclic anhydride appeared in 1850 cm^{-1} and 1778 cm^{-1} , but it disappeared in IR spectrum of hyperbranched polymer with terminal amidogen. In Figure 3 the strong absorptive peak of C=O in amide appeared in 1617 cm^{-1} . 2943 cm^{-1} and 2881 cm^{-1} belonged to characterized absorption peak of $-\text{CH}_2-$ was its symmetrical peak. The contrastive results and the appearance of amide groups indicated hyperbranched polymer with terminal amidogen had been obtained.

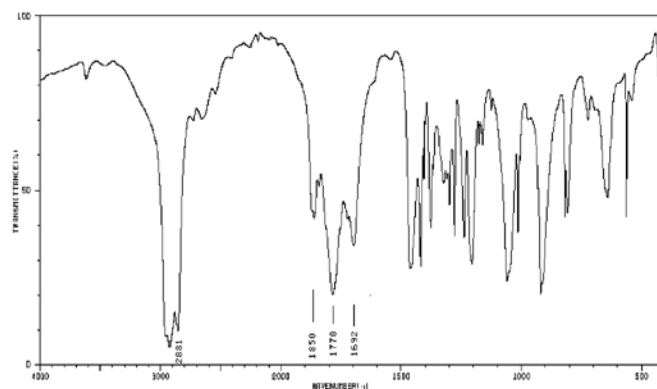


Figure 2: FT-IR spectrum of succinic anhydride

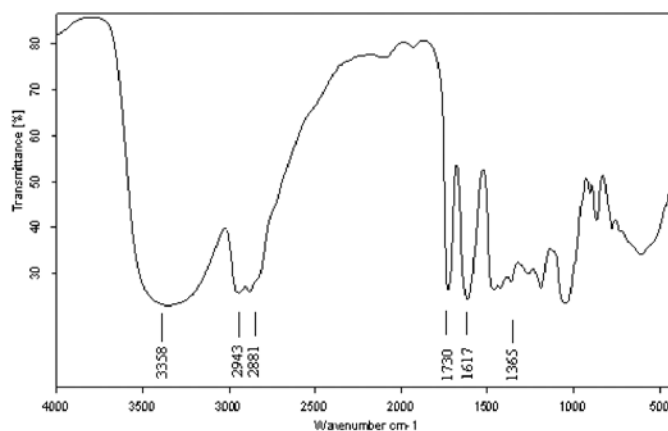


Figure 3: FT-IR spectrum of hyperbranched polymer with terminal amidogen

GPC analysis

GPC was a conventional method to detect the relative molecular weight of compound. Firstly the bigger molecule in chromatogram column would flow out, on the contrary, the small molecule was easy to flow into gel pore and slowly flow out from chromatogram column. Basing on the mechanism the relative molecular weight was determined. The relative molecular weight of hyperbranched polymer with terminal amidogen was shown in Figure 4.

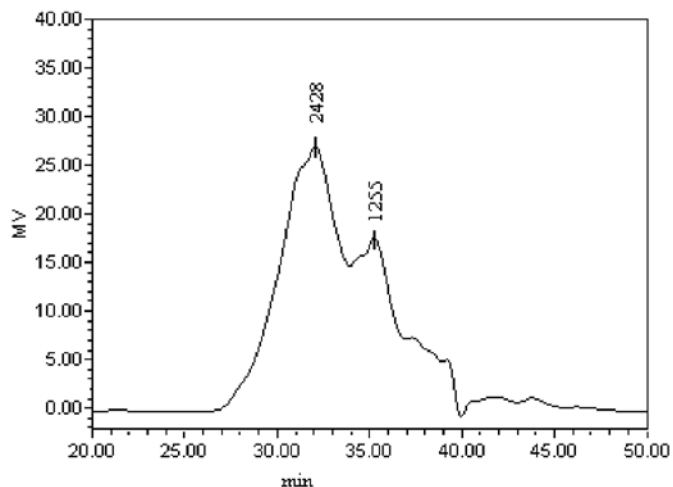


Figure 4: The GPC of hyperbranched polymer with terminal amidogen

As described in Figure 4, the distribution of relative molecular weight was even and it mainly included two parts. Its average relative molecular weight respectively was 2428 and 1255, and polydispersity was 1.394410 and 1.270659. In the study, “one-step” synthesis method was adopted, in other words, all reagents were put together and reacted, so hyperbranched polymer with different generations were obtained and it was normal for the product possessed different levels of relative molecular weight.²² Basing on divergent synthesis principle, they belonged to different generations. But in every generation their polydispersity nearly was 1, so the distribution of every generation was very well-proportioned.

Results of applying test

The formaldehyde-removal rate of formaldehyde scavengers and their effect on leather thickness and dye absorptivity were studied. The results were shown in TABLE II.

As indicated in TABLE II, the formaldehyde-removal rate of hyperbranched polymer with terminal amidogen was the best and it reached to 60.4%. The effect of 1, 6-hexanediamine and urea were less efficient than hyperbranched polymer with terminal amidogen. Furthermore, comparing with other formaldehyde scavenger, the thickening rate of hyperbranched polymer with terminal amidogen was the biggest. The hyperbranched polymer with terminal amidogen was a kind of macromolecule, so it had filling effect on leather which was similar with retanning agent.

CONCLUSIONS

A hyperbranched polymer with terminal amidogen was synthesized with succinic anhydride and diethylenetriamine by “one step method” and was characterized by FT-IR and GPC testing. From FT-IR spectrum of hyperbranched polymer with amidogen end-group, following conclusions were obtained. the overlapped peak of N-H bond in amide groups and amidogen was appeared in 3358cm^{-1} and the peak

of C=O in amide was in 1617cm^{-1} . These showed than the amidate reaction happened.

The hyperbranched polymer with amidogen end-group was characterized by GPC. Its average relative molecular weight respectively was 2428 and 1255, and polydispersity was 1.394410 and 1.270659. The distribution in every generation was very well-proportioned. The increase of relative molecular weight also indicated hyperbranched polymer with terminal amidogen had been synthesized.

The results of application experiment showed that the formaldehyde-removal rate of hyperbranched polymer with terminal amidogen reached to 60.4%. The formaldehyde content in leather was much less than limited value. Comparing with other formaldehyde scavengers, the thickening action and dye absorptivity of hyperbranched polymer with terminal amidogen respectively were 16.7% and 96.5%. So it was benefit for dye absorption and its filling effect on leather was obvious.

ACKNOWLEDGMENTS

The authors would like to thank the support of National Natural Science Foundation of China (20876090) and the doctoral foundation of educational ministry (20060708002).

REFERENCES

1. M. Breitsamer, O. Gotz. Emission from automotive leather-state of the art and a critical foresight. *JALCA* **99**, 416, 2004.
2. Leonardo S.G. Teixeira, Elsimar S. Leão, Aláilson F. Dantas, etal. Determiration of formaldehyde in Brazilian alcohol fuels by flow-injection solid phase spectrophotometry. *Talant*, **64**, 711, 2004.
3. S. Saravanabhavan, P. Thanakaivelan, J. Raghava Rao, etal. An enzymatic beamhouse process coupled with semi-metal tanning and eco-benign post tanning leads to cleaner leather production. *JALCA* **100**, 174, 2005.
4. J. Kanagaraj, S. Sadulla, M. Jawahar, etal. Interaction of aldehyde developed from amino acids of tannery waste in a lower-chrome tannage: an eco-friendly approach. *JSLT*, **89**, 18, 2004.
5. Qiang Xihuai, Tian Ling, Chen Guoping. Study on PAMAM's capturing ability of free formaldehyde in leather. *China Leather* **36**, 22, 2006.
6. Koizumi Mariko. Formaldehyde scavenger, methods for treatment woody plate, and woody plate. *Japanese patent*, 2002273145, 2002.
7. Rozynov B V, Coyle W J, Wood W E. Control of volatile carbonyl in compositions used in printing, printing methods and resulting printed structure. *US patent*, 6541560, 2003.

TABLE II
Contrast of formaldehyde-removal rate and the effect on leather properties

Formaldehyde scavenger	Formaldehyde content(mg/kg)	Formaldehyde-removal rate (%)	Dye absorptivity (%)	Thickening rate (%)
Blank sample	120	-	88.3	-
Hyperbranched polymer with terminal amidogen urea	47.5	60.4	96.5	16.7
Hydrogen peroxide	82.6	31.2	91.5	4.5
Sodium bisulfite	91.8	23.5	89.6	2.3
1,6-hexanediamine	93.8	21.8	87.5	1.8
	76.9	35.9	92.0	6.8

8. Rita Kakkar, Pramesh N. Kapoor, Kenneth J. Klabunde. Theoretical Study of the Adsorption of Fomaldehyde on Magnesium Oxide Nanosurfaces:size Effects and the Role of Low-Coordinated and Defect Sites. *J.Phys.Chem.B* **108**, 18140, 2004.
9. Fumihide Shiraishi, Shunsuke Yamaguchi, Yusuke Ohbuchi. A rapid treatment of formaldehyde in a highly tight room using a photocatalytic reactor combined with a continuous adsorption and desorption apparatus. *Chemical Engineering Science*, **58**, 929, 2003.
10. Dai Lan. The removal of free-formaldehyde in polyhydroxy resin. *Liaoning Environment Technology* **23**, 31, 2003.
11. Liu Chang-feng, Liu Xue-gui, Zang Shu-liang. Research Development of Free -formaldehyde Scavenger. *Liaoning Chemical Industry*, **33**, 331, 2004.
12. Smith, Richard D. Water-soluble blends of active methylene compounds and polyhydric alcohols as formaldehyde scavengers. *USA patent*, 5160503, 1992.
13. Pallab Banerjee, Wilfried Reichardt, Ralph Weissleder, Alexei Bogdanow.Jr. Novel Hyperbranched Dendron for Gene Transfer in Vitro and in Vivo. *Bioconjugate Chem* **15**, 960, 2004.
14. Chris Zhisheng Chen, Nora C. Beck-Tan, Prasad Dhurjati, Tina K.van Dyk, Robert A.Larossa and Stuart L.Cooper. Quaternary Ammonium Functionalized Poly (propylene imine)Dendrimers as Effective Antimicrobials: Structure-Activity Studies. *Biomacromolecules* **1**, 473, 2000.
15. Chao Gao, Deyue Yan, Bin Zhang, Wei Chen. Fluorescence Studies on the Hydrophobic Association of Pyrene-Labeled Amphiphilic Hyperbranched Poly(sukfone-amine)s. *Langmulr* **18**, 3708,2002.
16. Peter E., Froehling. Dendrimers and dyes-a review. *Dyes and Pigments* **8**, 187, 2001.
17. Ji Bing, Yang Jintian. Synthesis of terminal amido hyperbranched polyamide with succinic anhydride and diethylenetriamine. *Tonghua Teachers College Journal* **27**, 61, 2006.
18. Liu Xiankui. Study on the determination of formaldehyde content in leathers and furs. *China Leather* **32**, 18, 2003.
19. Yu Congzheng, Ding Shaoan, Sun Genxing. Leather analysis and test. Chemical publishing company, *Beijing*, 2005.
20. H. Ozgunay, O. Sari, M. Tozan. Molecular investigation of valonea tannin. *JALCA* **102**, 154, 2007.
21. Nakagawa, K., Sugita, M. Spectroscopic characterization and molecular weight of vegetable tannins. *JSLTC* **83**, 251,1999.
22. Peter E.Froehling. Dendrimers and dyes-a review. *Dyes and Pigments*, **8**, 187, 2001.