ISSN : 2249 - 8877 Volume 6 Issue 3

Research & Reviews On Polymer

Full Paper

RRPL, 6(3), 2015 [118-131]

Functional polyethers for fixing pigments on cotton and wool fibres

Ahmed G.Hassabo[1]*, Michael Erberich[2], Crisan Popescu[2], Helmut Keul[2]

[1]National Research Centre (Scopus afflitiation ID 60014618), Textile Research Division, Pre-treatment and Finishing of Cellulosic Fibers Department, El-Behouth St. (former El-Tahrir str.), Dokki, P.O. 12622, Giza, (EGYPT)

[2]DWI an der RWTH Aachen and Institute of Textile Chemistry and Macromolecular Chemistry (ITMC), Aachen University, Forckenbeckstrasse50, D-52056 Aachen, (GERMANY)

E-mail: aga.hassabo@hotmail.com

ABSTRACT

The present work describes an alternative to traditional dyeing of cotton and wool by using their coating with pigments. An application to the surface in general entails the risk of a slight down-washing of the dye from the fibre surface. To circumvent this problem, a random copolymer is synthesized by the use of Allylglycidylether and Ethoxyethylglycidylether as starting materials. This copolymer is converted by hydrolysis, modification with dimethylaminopropylamine and 3-aminopropyl-tris (trimethylsiloxy) silane and final quaternization with methyl iodide in a cationic polymer, into a binding agent between the fibre and pigment. The SEM examination of the results of applying the copolymer complexed with a fluorescent pigment on to cotton and wool shows that the coating layer on cotton is, generally, more consistent than on wool fibres, in line with the different electric charge distribution along the fibre surfaces. These observations allows us proposing the optimum pH range for utilization of the polymer-pigment complex in coating operation as being of 7…9, for 30 minutes at 50°C for wool and 90°C for cotton, respectively.

KEYWORDS

Coating;
Pigment;
Allylglycidylether;
Ethoxyethylglycidylether;
Natural fibres

INTRODUCTION

Cotton and wool, the most used natural fibres,keep a large share of the total fibres used for apparels and the growing demand of green and renewable materials is helping this trend.

Cotton, the most utilized fibre for garments,is made mainly of highly crystalline cellulose, some wax and protein components. Fibre surface hasonly hydroxyl groups, as cellulose is exclusively formed from Cellobiose units (disaccharide composed of two glucose units, glycosidically linked by 1, 4-link)[1-4].

Wool is a keratin fibre, consisting of proteins made of chains of amino-acids. The fibre surfacehasdifferent functional groups, because of different side groupsof the amino-acids[5-8].

The dyeing of natural fibres starts with bleaching for achieving a clean, white substrate, followed by up-taking of dyes from solution and their diffusion and fixation into fibre[9-12]. The disadvantage of

this procedure is the large amount of various chemicals from bleaching and colouring which go into effluents, polluting heavily the waters.

Another approach consists in applying pigment onto the surface of the fibre. This corresponds to "painting" of the fibre. The advantage of this method is that the colouring agent may be applied without any prior treatment and this reduces the necessity of the aggressive treatment of bleaching.

Since pigments do not adhere to fibre surfaces, a type of binding agent must be developed. To achieve this, the primer must coordinatechemically with both the fibre and the dye, so that the best possible interaction is achieved.

The aim of this work is the development of a functional polyether which is able to fix pigments permanently to fibres. The polyether appears of particular interest because it provides several functional groups: i) Cationic groups, ii) Cross-linkable groups and iii) Hydrophobic groups.

Hydrophobic groups affect the adjustment of the solubility of the primer. While cationic groups are often hydrophilic and therefore lead to a relatively high solubility in water, additional hydrophobic groups cause a decrease in the solubility in water, leading to better interaction with surfactants.

In addition, the polymers should be cross-linked. This brings the advantage that when the polymers are cross-linked after application on the fibres they form a durable dye-polymer complex.

EXPERIMENTAL

Materials

Diglyme (Alfa Aesar, 99%) was dried over sodium, distilled under reduced pressure and stored on molecular sieves 4 Å. Ethoxyethylglycidylether (EEGE) was synthesized according to Fitton *et. al.*[13], glycidol (Aldrich, 99%), ethyl vinyl ether (Aldrich, 99%) and p-toluenesulfonic acid monohydrate was used without further purification for the synthesis. Allyl glycidyl ether (AGE)(Fluka, 99%) was dried over CaH_2,distilled under reduced pressure and stored on molecular sieves 4 Å. 3-Dimethylamino-1-propyl amine (DMAP) and (3-aminopropyl) tris (trimethylsiloxy) silane (SILO), and methyl iodide was used without further purification. Other solvents were used in technical purity.

Measurements

^{1}H NMR spectra (300 MHz) and ^{13}C NMR spectra (75 MHz) were recorded using a Bruker DPX 300 spectrometer. All measurements were performed at room temperature. Either $CDCl_3$ or DMSO-d_6 was used as solvent. As an internal standard for the measurement in $CDCl_3$ tetramethylsilane (TMS) was used; the measurements in DMSO-d_6 and in all analyses of silicon-containing products, the residual signal of the solvent was used as internal standard, at a chemical shift of δ = 2.50 ppm for DMSO and δ = 7.27 ppm for $CHCl_3$. All ^{13}C NMR spectra were recorded using the ^{1}H broadband decoupled modus. Coupling constants J are given in Hertz (Hz). The fine structure of the resonance signals represented by the abbreviations s (singlet), d (doublet), t (triplet), quart (quartet), m (multiplet) and br (broad).

Gel permeation chromatography (GPC) measurements were performed on two different systems. Using N, N-dimethylacetamide (DMAc, with 2.441 g/l of LiCl) as eluting solvent, a high pressure liquid chromatography pump (Bischoff 2250) and a refractive index detector (Waters 410, Millipore) at 80°C were used at a flow rate of 0.8 mL/min. Three chromatography columns with DVB- gel from MZ analysis technique were used, the length of the columns was 300 mm, the diameter of the column 8 mm, the diameter of the gel particles was 5 ?m and the nominal pore width were 100, 1000 and 10000 Å. Using tetrahydrofuran (THF, 250 mg/l BHT) as eluent a high pressure liquid chromatography pump (ERC HPLC 6420) and a refractive index detector (Jasco 2031plus) at 20°C were used at a flow rate of 1.0 mL/min. Four chromatography columns, with the DVB- gel from MZ analysis technique was used, the length of the columns was 300 mm, the diameter of of the columns was 8 mm, the diameter of the gel particles was 5 ?m and the nominal pore width were 50, 100, 1000 and 10000 Å. Calibration was performed either with PMMA or with PS standards from Polymer Laboratories (as indicated at the appropriate place). The number average molecular weight, the weight average molecular weight and polydis-

persity M_w/M_n were determined using the software program package, NTeqGPC V6.01.18.

Syntheses

Synthesis of poly[(allylglycidylether)-co-$_{15}$(ethoxyethylglycidyl ether)$_{27}$](1)

3-Phenyl propanol (328 mg, 2:41 mmol) and KO*t*Bu (1M in THF, 0.24 mL) in diglyme (absolute, 25 mL) were added to a dried 100 mL Schlenk flask and stirred for about 20 min at 40°C. The resulting *t*BuOH was then removed in vacuum.

The monomer mixture composed of AGE (4.846 g, 42.40 mmol) and EEGE (11.012 g, 75.33 mmol) was prepared in a 50 mL Schlenk flask. The composition of the monomer mixture was analysed using ^{1}H NMR spectroscopy (Result: nEEGE: nAGE ≈ 1.78). The monomer mixture (15.510 g) was added to the initiator solution and stirred at 120°C for 21 h. Then the solvent was removed by distillation at 80°C. The reddish oily residue was dissolved in dichloromethane (75 mL) and washed with saturated NaCl solution, 75 mL). The organic phase was collected and the aqueous phase was washed with fresh dichloromethane (3 × 50 mL). The combined organic phases were dried over K_2CO_3, filtered, concentrated on a rotary evaporator, anddried in vacuum overnight to afford the yellow oily product in a yield of 16.245 g (100 %).

The ^{1}H NMR analysis showed: m = 15, n = 27 (n/m = 1.8, corresponds to the ratio of the monomers in the feed).

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.19 (t, ^{3}J = 7.03 Hz, 3H, CH_3-17), 1.29 (d, ^{3}J = 5:09 Hz, 3H, CH_3-15), 1.83 - 1.93 (m, 2H, CH_2-6), 2.65 - 2.70 (m, 2H, CH_2-5), 3:43 - 3.70 (m, 9H, CH-9, CH_2-7/8/10/16), 3.98 (d, ^{3}J = 5:27 Hz, 2H, CH_2-11), 4.70 (quart, ^{3}J = 5.20 Hz, 1H, CH-14) 5:21 (dd, ^{2}J = 31.25 Hz, 3J = 13.80 Hz, 2H, CH_2-13), 5.82 - 5.95 (m, 1H, CH-12), 7:17 to 7:19 (m, 3 H, CH -1/3), 7:25 to 7:30 (m, 2H, CH_2) ppm.

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 15:31 (C-17), 19.79 (C-15), 60.78 (C-16), 70.00 - 70.26 (C-8), 71.92 (C-10); 72.24 (C-11), 78.80, 78.91 (C-9), 99.69, 99.82 (C-14), 116.68 (C-13), 125.76 (C-1), 128.30, 128.43 (C-2/3); 134.89 (C-12) ppm.

GPC (DMAc): M_n = 4600 M_w/M_n= 1.11 (pMMA-Standards)

Synthesis of poly[(allyl glycidyl ether)$_{15}$-co-(glycidol)$_{27}$](2)

Poly [(allyl glycidyl ether)-co-(ethoxy ethylglycidyl ether)$_{27}$] (3.010 g, 2.14 mmol acetal) was added to a 500 mL single-necked flask containing technical THF (300 mL). After complete dissolution an aqueous HCl solution (37%, 20 mL, 240 mmol) was added and stirred at room temperature for 20 min. Subsequently, the solution was dried and neutralized in portions withpotassium carbonate. After filtration, and concentration of the solution on a rotary evaporator the oily residue was dried in vacuum over night at 45°C. The product was obtained as a reddish oil in a yield of 1.779 g (92%).

^{1}H- NMR (DMSO- d_6, 300 MHz): δ = 1:46 to 1:55 (m, 2H, CH_2-6), 2:57 - 2.62 (m, 2H, CH_2-5), 3:35 to 3:58 (m, 7H, CH -7, 8, 10, CH-9), 3.93 (d, 3J = 4:15 Hz, 2H, CH_2-11), 4.99 (brs, 1H, OH), 5:17 (dd, 2J = 34.03 Hz, 3J = 13.82 Hz, 2H, CH_2-13), 5.79 - 5.92 (m, 1H, CH-12), 7:12 to 7:18 (m, 3H, CH-1, 3), 7:23 to 7:28 (m, 2H, CH_2) ppm

GPC: M_n (DMAc) = 7200 M_w/M_n=1.12 (pMMA-St.)

Synthesis of poly (allyl glycidyl ether)$_{15}$-co-(phenoxycarbonyl glycidyl ether)$_{27}$](3)

A solution of the deprotected polymer poly[(allyl glycidyl ether)$_{15}$-co-(glycidol)$_{27}$] (1.807 g, 14.0 mmol of OH groups) and triethylamine (1.583 g, 15.6 mmol, 1.11 eq) in THF (15 mL) was added under ice-cooling within 15 min to a solution of phenyl chloroformate (2.724 g, 17.4 mmol 1.24 eq) in THF (15 mL). After completion of the addition, the ice bath was removed and the reaction mixture was warmed to room temperature. Stirring was continued at room temperature for 18 h. For work up the reaction mixture was diluted with dichloromethane (40 mL) and washed first with an aqueous solution of HCl (1 M, 2 × 50 mL) and saturated aqueous NaCl solution (70 mL). was treated with and diluted with pure water (50 ml). The organic phase was dried over Na_2SO_4 and concentrated on a rotary evaporator. From this concentrated solution, the polymer wasprecipitated in pentane (250 mL). The precipitate was dried in vacuum over night at 45°C.

The product was obtained in a yield of 1.763 g (50.5 %).

^{1}H -NMR ($CDCl_3$, 300 MHz): δ = 1.88 (br, 2H, CH_2-6), 2.65 - 2.69 (m, 2H, CH_2-5), 3.25 - 3.70 (m, 7H, CH-9, CH_2-7/8/10), 3.97 (br, 2H, CH_2-11); 4.28 (br, 1H, CH_2-14); 4:41 (br, 1H, CH_2-14); 5:14 to 5:28 (m, 2H, CH_2-13); 5.87 (br, 1H, CH-12), 7:16 to 7:35 (m, 10H, CH-1/2/3/17/18/19) ppm.

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 69.20 - 70.35 (C-7/8/10/14), 72.22 (C-11), 78.60 - 79.13 (C-9); 116.80 - 117.06 (C-13), 120.95 (C-17), 125.97 (C-1/19), 128.37 (C-2/3), 129.40 (C-18), 134.62, 134.71 (C-12), 151.02 (C-16); 153.50 (C-15) ppm. Signals for C-4, C-5 and C-6 are not found.

GPC (DMAc): M_n= 7000 M_w/M_n = 1.50 (pMMA-St.)
M_n= 9000 M_w/M_n = 1.41 (pS-St.)

Reaction of poly[(allylglycidyl ether)$_{15}$-co-(phenoxycarbonylglycidyl ether)$_{27}$] with amines (4)

Poly[(allyl glycidyl ether)$_{15}$-co-(phenoxycarbonylglycidyl ether)$_{27}$] Poly[(AGE)$_{15}$-co-PCGE)$_{27}$] (3) (3.241 g, 13.1 mmol of carbonate groups) was dissolved in technical THF (20 mL). A mixture of DMAPA (1.075 g) and SILO(1.508 g) (according to ^{1}H NMR analysis DMAPA/SILO = 2: 1) are stirred for 3 days at room temperature. To the reaction mixture dichloromethane (130 mL) was added and washed with aqueous NaOH solution (1 M, 3 × 50 mL). The organic phase was dried over Na_2CO_3, filtered and concentrated on a rotary evaporator. Drying overnight gave the product in a yield of 3.657 g (83.6 %).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0:10 (s, 27H, CH_3-23); 0:41 to 0:47 (m, 2H, CH_2-22); 1:41 to 1:56 (m, 2H, CH_2-21), 1.63 - 1.67 (m, CH_2-17); 2.20 (s, 6H, CH_3-19), 2.31 (t, ^{3}J = 6.83 Hz, 2H, CH_2-18); 3:11 to 3:20 (m, 4H, CH_2-16/20); 3:45 - 3.77 (m, 7H, CH-9, CH_2-7/8/10); 3.98 - 4:22 (m, 4H, CH_2-11/14); 5:15 to 5:29 (dd, 3J = 13.72 Hz, ^{2}J = 28.54 Hz, 2H, CH_2-13), 5.82 - 5.95 (m, 1H, CH-12), 7:13 to 7:19 (m, 3H, CH-1/3); 7:25 to 7:29 (m, 2H, CH_2) ppm.

^{13}C NMR (75 MHz, $CDCl_3$): δ = 1.67 (C-23), 11:40 (C-22), 25.53 (C-17/21), 45.38 (C-19), 67.88 (C-14); 69.20 - 70.18 (C-8/10), 72.20 (C-11), 116.79 (C-13), 126.57 (C-1), 128.39 (C-2/3), 134.64 - 134.74 (C-12), 156.47 - 156.54 (C-15) ppm.

GPC (DMAc): M_n = 9000 M_w/M_n =1.65 (pMMA-St.)

Quarternization of the polyether with dimethylaminopropyl-urethane and tris(trimethylsiloxy)-silyl-propan-urethan (functionalized Polyethers) (5)

The urethane functionalised polyether4 (2.383 g, 5.0 mmol dimethylamino groups) was dissolved in methanol (10 mL) and treated with a solution of methyl iodide (7.155 g, 50.4 mmol, 10 eq of MeI) in methanol (10 mL). The solution was stirred for 24 h at room temperature. Finally, the solvent and excess methyl iodide was removed on a rotary evaporator and the residue dried overnight in vacuum at 45°C. The product was obtained as yellow, powdery solid. Yield 2.724 g (88 %).

^{1}H NMR (methanol -d_4, 300 MHz): δ = 0:19 (br, 9 H, $SiMe_3$), 0.69 (br, 2 H, CH_2-22); 1.64 - 1.90 (br, 4 H, CH_2-20/21), 2.10 (br, 2 H, CH_2-17); 3:28 to 3:38 (m, 13 H, CH_2-16/18, CH_3-19), 3:58 - 3.75 (m, 7 H, CH -9, CH_2-7/8/10), 4:07 to 4:25 (m, 4 H, CH_2-11/14), 4.84 (br, 1 H, NH), 5:24 to 5:37 (m, 2 H, CH_2-13); 5.97 (br, 1 H, CH-12), 7:25 to 7:31 (m, 3 H, CH-1/2/3) ppm.

^{13}C NMR (methanol -d_4, 75 MHz): δ = 02.18 (C-23), 25.00 (C-17), 54.22 (C-19), 65.74 (C-10), 80.25 (C- 9), 71.34 (C-11), 73.37 (C-8), 117.45 - 117.62 (C-13), 136.37 (C-12), 158.72 (C-15) ppm. Other signals are not visible.

Preparation of the polymer/silica suspension

Polymer 5 (500 mg) was dissolved in water (5 mL). The resulting oily suspension was stirred vigorously overnight. During this time, the polymer dissolves completely. Subsequently, 3 mL of silica pigment suspension was added at room temperature with stirring for about 10 min to produce a new suspension.

RESULTS AND DISCUSSION

The present work aims at investigating the use of poly-ethers to anchoring pigments on heteroge-

neous surfaces of natural fibres. For this purpose the poly-ethers are designed with groups able to bind both the colouring molecules (pigments) and the functional groups from the surfaces of cellulosic (cotton) and keratin (wool) fibres.

Synthesis and characterization of the copolymers

The functional polyether, which meets the above criteria, is composed of at least two building blocks, which can be selectively addressed in post polymerization modification reaction. A suitable option is a linear copolymer of glycidol, as described in the literature[14-17]. The advantage of polyethers in general and of polymers having a polyethylene glycol backbone in particular, consists in the flexibility of the polymer backbone, which is facilitated by the ether oxygen atom, in contrast to the more rigid polyolefins. This flexibility ensures a good interaction of the polymer back bone and of the side chains with rough surfaces.

Polyethers based on glycidolmonomers with orthogonal protecting groups have the advantage that a selective deprotection followed by functionalization allows the preparation of multifunctional polyethers. The corresponding functional polyether cannot be obtained by direct polymerization of the corresponding monomers due to mechanistic incompatibility[17].

The first monomer is a glycidol derivative - allyl glycidyl ether (AGE) with an allyl side groupwhich is stable under alkaline and acidic conditions. The second monomer with an acetal protecting group (ethoxyethylglycidylether, EEGE[18]) was chosen due to the easy removal of the acetal protecting group under acidic conditions. Consequently a copolyether with allylic and acetal side groups yields quantitatively and in short time primary alcohol groups under acidic conditions resulting in a water soluble polyether with allylic side groups. The allylic side groups can be further used for the formation of networks and the hydroxyl groups can be modified in post polymerization modifications to introduce cationic and hydrophobic groups, which themselves can be used for functionalization of surfaces.

3-Phenyl propanol was selected as initiator for the polymerization of mixtures of EEGE and AGE. The phenyl propanol end groups allow determination of the degree of polymerization by end group analysis using ^{1}H NMR spectroscopy;signals of the initiator do not overlap with signals of the repeating units[14-17].

Starting with poly(allyl glycidyl ether)-co-(ethoxy ethyl glycidyl ether) the necessary functions are introduced by post polymerization modification reaction. First, the primary alcohol groups are generated by acid catalysed hydrolysis and then quantitatively converted to phenylcarbonat groups. Additional functionalities are introduced by reacting the activated phenylcarbonate groups with suitable functionalized amines.3-Dimethylamino-1-propyl amine (DMAPA) and (3-aminopropyl) tris (trimethylsiloxy) silane (SILO) were selected as functional amines. DMAPA serves as a precursor for cationic groups, while SILO provides hydrophobic groups and the possibility to covalently link the polymer to surfaces with free hydroxyl groups. In Figure 1 the building blocks for the final multifunctional polymer are shown.

A linear, statistical copolymer consisting of allyl glycidyl ether and ethoxy ethyl glycidyl ether in molar ratio of AGE/EEGE = 1 : 2 was prepared by anionic ring-opening polymerization with 3-phenyl

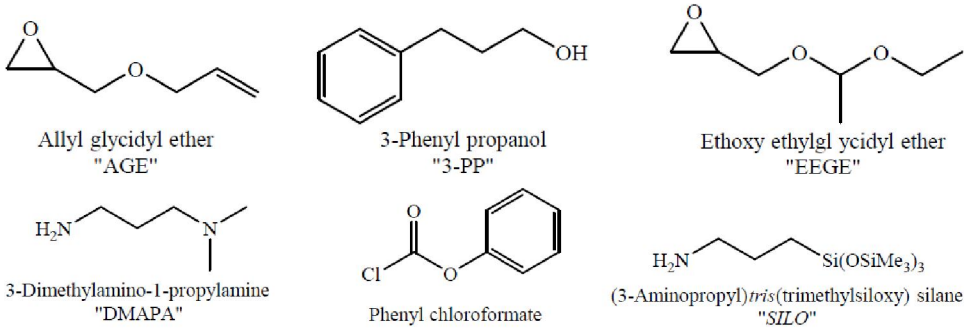


Figure 1 : Buildingblocks usedfor the synthesisof the target copolymer

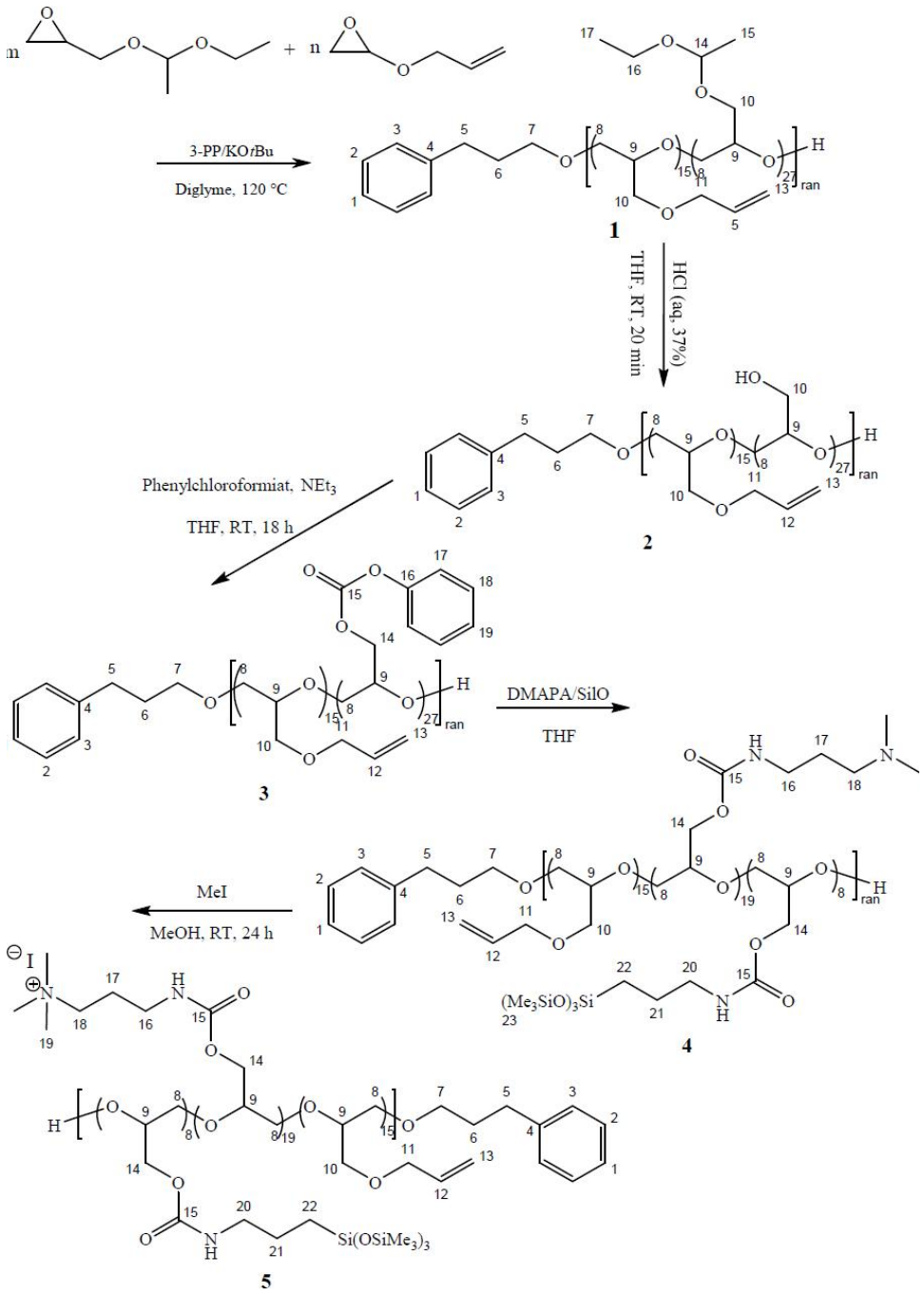


Figure 2 : Synthesis of the multifunctional polyether; (1) poly[(allylglycidylether)$_{15}$-co-(ethoxyethylglycidylether)$_{27}$], (2) poly[(allyl glycidyl ether)$_{15}$-co-(glycidol)$_{27}$], (3) poly[(allylglycidylether)$_{15}$-co-(phenoxycarbonylglycidylether)$_{27}$], (4) multifunctional polyglycidol, (5) multifunctional polyglycidol with quaternary ammonium- and tris(trisilyloxy) silane side groups

propanol as initiator (Figure 2). The initiator is activated with potassium tert-butoxide (KOtBu) and a total degree of polymerization of P_n = 45 was adjusted by the monomer to initiator ratio.

The microstructure and the degree of polymerization of the copolymer were confirmed by ^{1}H-NMR spectroscopy. In addition, on the one hand the ratio of the repeat units was determined by comparing the signals for the acetal-CH at δ = 4.7 ppm, and the allyl CH at δ = 5.9 ppm and on the other hand, these signals to a CH_2 signal of the initiator at δ = 2.7 ppm correlated (Figure 3). The result of this analysis is AGE / EEGE = 15 / 27. The total degree of polymerization reached 42, and that is in good agree-

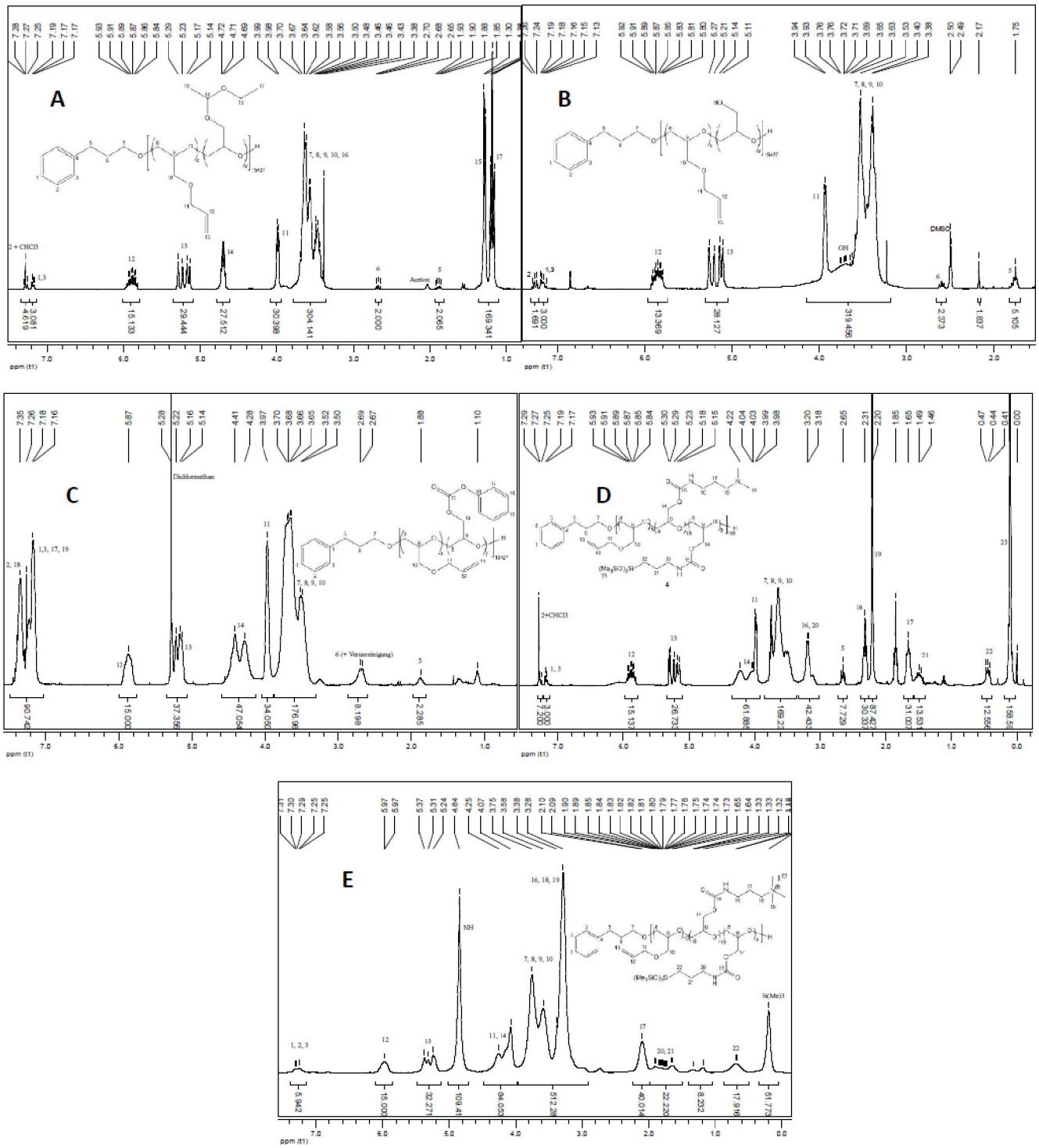


Figure 3: ^{1}H-NMR spectraof differently substituted polyether; A) poly[(allyl glycidyl ether)$_{15}$-co-(ethoxy ethyl glycidyl ether)$_{27}$] (1) in $CDCl_3$, B) poly[(allyl glycidyl ether)$_{15}$-co-(glycidol)$_{27}$] (2) DMSO-d_6, C) poly[(allyl glycidyl ether)$_{15}$-co-(phenoxy carbonyl glycidyl ether)$_{27}$] (3) in $CDCl_3$, D) multifunctional polyglycidol (4) in $CDCl_3$, E) multifunctional polyglycidol with quaternary ammonium- and tris(trisilyloxy) silane side groups (5) in methanol-d_4

ment with the theoretical degree of polymerization. Characteristic forthe polyglycidol backbone is the broad signal at δ = 3.4 - 3.7 ppm[14-17].

The GPC analysis of poly (AGE-co-EEGE) (1) and poly (AGE-co-G) (2) (Figure 4) also showed a relatively narrow molecular weight distribution on (M_w/M_n = 1:11 for 1, M_w/M_n = 1:12 for 2) as is expected for controlled polymerizations. These results

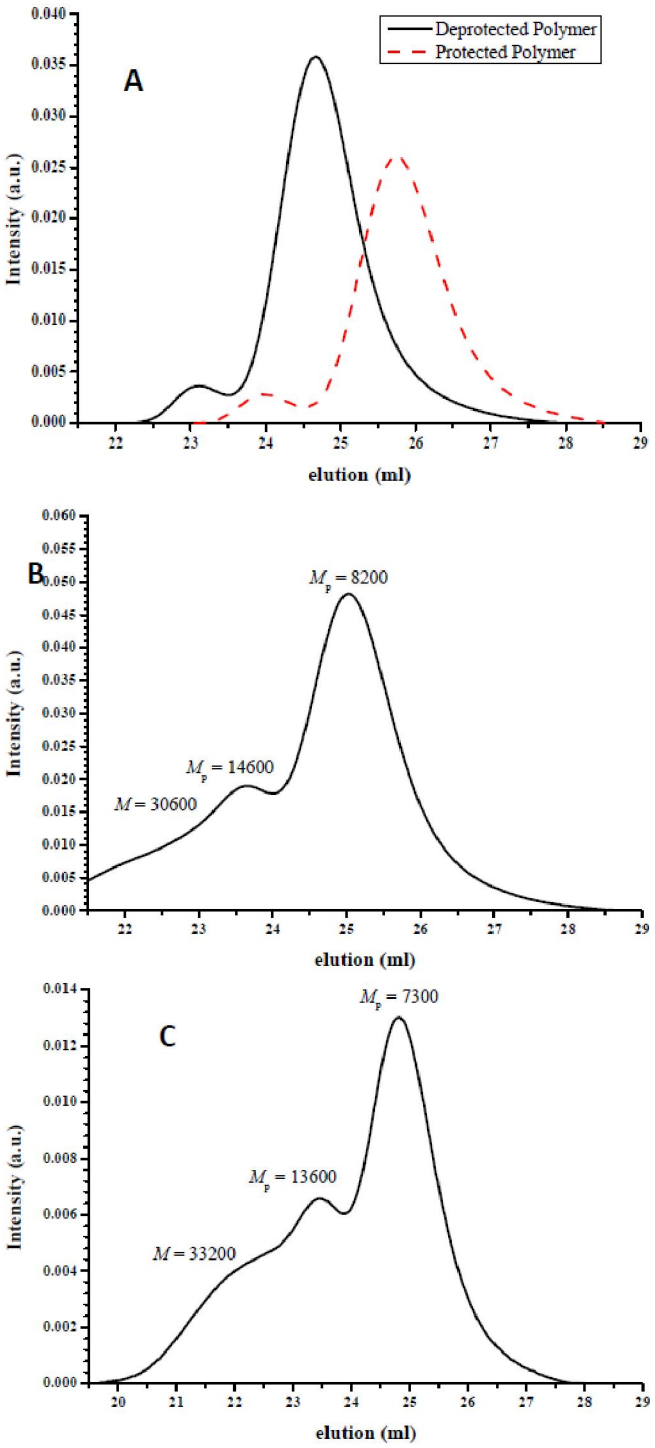


Figure 4 : GPCeluograms measured inDMAcas eluent; A) dotted red line: poly[(allyl glycidyl ether)$_{15}$-co-(ethoxy ethyl glycidyl ether)$_{27}$] (1); black line: poly[(allyl glycidyl ether)$_{15}$-co-(glycidol)$_{27}$] (2); B) poly[(allyl glycidyl ether)$_{15}$-co-(phenoxycarbonylglycidyl ether)$_{27}$](3) C) multifunctional polyglycidol (4)

show that the polymerization of this monomer mixture is both controlled and proceeded quantitatively. Since both monomers react with similar rates a random copolymer is obtained[19].

The removal of the acetal-protecting group was carried out by acid hydrolysis in tetrahydrofuran (Figure 2). The product poly(allylglycidylether-co-glycidol) (2) was obtained in quantitative yield; the allylic protecting group remains intact[17], which is confirmed by the ^{1}H NMR spectrum, too (Figure 3B). GPC analysis also indicated complete deprotection; the shape of the eluogram is similar to the starting polymer, however the molecular weight is shifted to higher values (Figure 4).

Polymer 2 prepared in this way was then converted with phenylchloroformate in THF and triethyl amine as acid scavenger to yield poly(allylglycidylether)-co-(phenoxycarbonylglycidyl ether) (3) (Figure 2). Conversion of the hydroxyl groups was quantitative as shown by ^{1}H NMR analysis (Figure 3C); all hydroxymethyl groups were converted to phenyl carbonate groups. Comparison of the signal of the allylic groupsat δ = 5.87 ppm with the newly formed signal of the CH_2 group in α -position to the phenyl carbonate group - double peak at δ = 4:28 and δ = 4:41 ppm –revealed that the ratio of the corresponding integrals corresponds to the ratio of the repeating units in the original polymer2. Itshould be noted that the occurrence of two peaks for signal 14 is characteristic for this structure. The product was isolated in high purity but only in a yield of about 50%.

GPC analysis of polymer 3 in N, N-dimethylacetamide showed a bimodal distribution (Figure 4B). We assume that the reaction of phenyl chloroformate and polyglycidol repeating units leadstochain couplings (Figure 5).

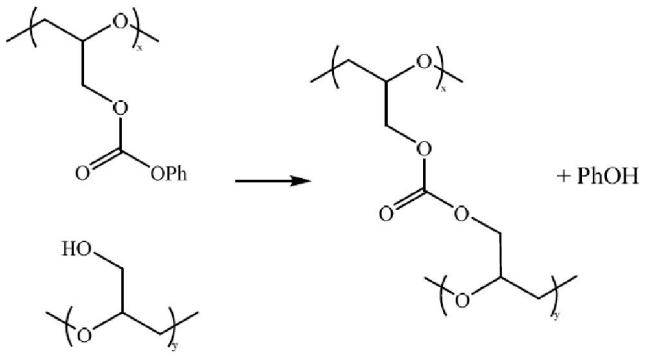


Figure 5 : Possiblecoupling reaction betweentwochains duringfunctionalizationof polyglycidolwithphenyl chloroformate

Full Paper

The post polymerization reaction of activated phenyl carbonates with functional amines leads to the formation of urethane groups and elimination of phenol. Functionalization was carried out in THF with a mixture of the two amines DMAPA and SILO.

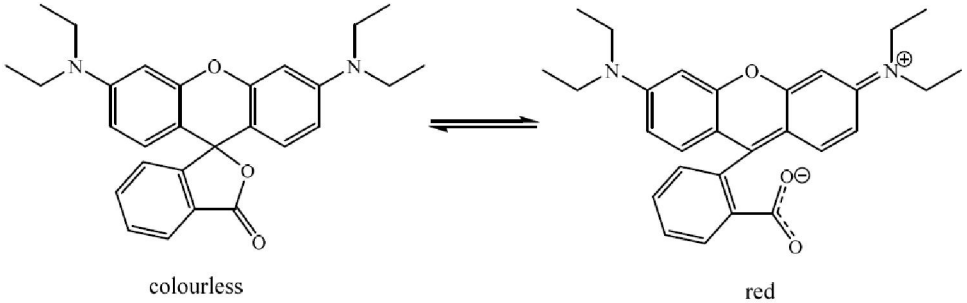
The ratio of the amines used was varied; first, an equimolar mixture of the two amines was used. As product, a viscous material was obtained under these conditions, which proved to be insoluble in common organic solvents. As a consequence, determination of the degree of functionalization by ^{1}H NMR spectroscopy was not possible. Insolubility also prevented further investigation. From this result it was assumed that crosslink occurs by the formation of Si-O-Si groups andis related to the concentration of tris(trimethyl silyloxy)-silane groups within the polymer[20]. By decreases the concentration of SILO to a ratio of DMAPA / SILO = 2: 1 the cross-linking could be prevented (Figure 2). According to ^{1}H - NMR analysis (Figure 3D) the ratio of the two amines in the copolymer corresponds with the ratio of the two amines in the feed. The multifunctional polyether 4 was used in the last step for quaternization of the tertiary amine groups introduced. The GPC elugram of the product shows a similar trace as that of the starting polymer3 (Figure 4C). This result proves full conversion of the starting material. An alternative explanation of the multimodality of the GPC curve is that in the reaction with the amines polymers of different composition are formed, so that the distribution of chain length overlaps with the distribution of functionalities.

Quaternization of the dimethylamino groups of polyether 4 to trimethylammonium groups was carried out in methanol with an excess of methyl iodide (Figure 2). According to the^{1}H - NMR analysis, functionalization proceeded quantitatively as resulted from comparison of the signals for the allyl group (δ = 5.97 ppm, CH) with the signals for the trimethylsilyl group (δ = 0.19 ppm) and the quaternary ammonium group (R-$^+$NMe$_3$, δ = 3:28 ppm (Figure 3E)). Multifunctional polyether5 was obtained quantitatively as a yellow powder. This product was soluble in water, however, the dissolution rate is relatively low; at the beginning an emulsion is observed, which by stirring overnight forms a yellow solution.

Application of the copolymers of poly [(allylglycidylether)$_{15}$-co-(3-(tri methyl ammonium) propylglycidylcarbamat)$_{18}$-co-(3-(tris-methyl-siloxy) silanyl-propylglycidylcarbamat)$_9$] (5) silica pigments

To investigate the applicability of the Polymer 5 with respect to fibres and pigments, silica pigments from Post Nova Analytics were acquired. The pigments have a spherical, non-porous shapeof an average diameter of 300 nm, with a surface covered with carboxyl functionalities. The concentration of the carboxylic acid functions in the aqueous suspension was 1 mol/mL, the solid content was 50 mg/mL, and the particle concentration was 1.8×10^{12} mL^{-1}. The particles were dyed red withRhodamine B whose structure is shown in Figure 6 as leuco base and quinoid coloured form.

In a 10% aqueous solution of Polymer 5 was added the suspension of the silica pigment andthe polymer/pigment-complex was diluted to a 2% suspension with water. Cotton and wool fibres were



Rhodamin B, $C_{28}H_{30}N_2O_3$, Mol. Wt.: 442,55
3',6'-bis(diethylamino)-3*H*-spiro[isobenzofuran-1,9'-xanthen]-3-on

Figure 6 : Chemical Structure and colour shifting of RhodamineB

immersed in this suspension at pH values ranging from 3 to 9 for 30 minutes at temperature specific for each fibre.

The ratio fibre to suspension (liquor ratio) was in each case 1: 100 which means that for 1 g fibre in 100 mL of solution was used. The treated fibres were dried and examined.

Fluorescence measurements

Fluorescence of Polymer (5), silica pigments and of their mixture was measured by usinglight of 200 - 900 nm wavelengths for irradiating and detecting the wavelength of the emitted light.

The maximum emission (identical to the maximum of the absorption) was for all three samples at about 470 nm. In all samples two fluorescence maxima are recorded, of which the first one at about 387 nm (Ex 1, TABLE 1), and the second maximum in the visible spectrum at 560…570 for the Polymer and Pigment, respectively and at a significantly lower wavelength (500 nm) for the polymer/pigment mixture (Ex 2, TABLE 1). One may thus assume that the silica pigments formed a chemical complex rather than a mechanic mixture with the Polymer.

Application of the particle/polymer complex to fibres

The aim of the study is to achieve applying fluorescent pigments on different natural fibres and to determine the optimal parameters for this process.

The natural fibres considered are cotton and wool. The pH was adjusted in each case to the values of 3, 5, 7 and 9, respectively, in order to investigate the pH dependence of the coating layer. Cotton was treated at 90°C, and wool at 50°C for 30 min in all the cases.

The optimal conditions for coating cotton are expected to be met at values of pH above 7. At pH values in the acidic range it is expected that the glycosidic bonds between the cellulose units of the cotton fibres hydrolyse and lead to the weakening of the fibres. As a consequence the coating of cotton in the acidic range of pH is of a low practical interest.

Wool fibres behave contrary to cotton ones, preferring acidic pH values for a treatment and being degraded when pH values go above 7. As a result the optimum pH for coating keratin fibres is in the acidic range.

On the other side it is also known that the fibres have specific surface charges at various pH values[21,22]. Keratin surface is positive at pH values below 3-4 and negatively charged for higher pH-values; cotton fibre surface is negative for almost all pH-values, and turns positive only in very acidic range[23]. This means that the positively charged polymers areable to adhere to both of the fibres over a large range of pH values, providing the pH values favours also a good protection to fibre structure (Figure 7).

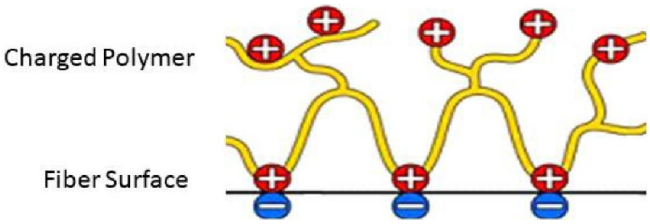


Figure 7 : addition of apositively chargedpolymerto a negatively chargedsurface ofthe fibre, pH <7

Cotton fibre

The SEM pictures of untreated cotton fibre (Figure 8) showthe smooth structure of the surface. Themechanical attachment appears virtually impossible; hence any addition of colouredparticles occurs only by relevant interactions, related to the chemical interaction.

As the SEM images of the cotton fibres treated at the four different pH values show the coating density of the polymer/dye complex on cotton is always quite high. Contrary to the expectations, even at the low pH-value (3) there is a relatively good coating with pigments; the level of coating is only increased by increasing the pH values of the treatment.

As expected, the largest coating layers were found at pH = 7 and pH = 9, respectively. This range is also of interest from technological point of view, as cotton structure is better protected at such pH-values.

Compared to wool the density of coating layeron cotton is significantlylarger, even when a low concentration of pigments is used(stock solution of 2%)at a liquor ratio of 1: 100. This indicates that

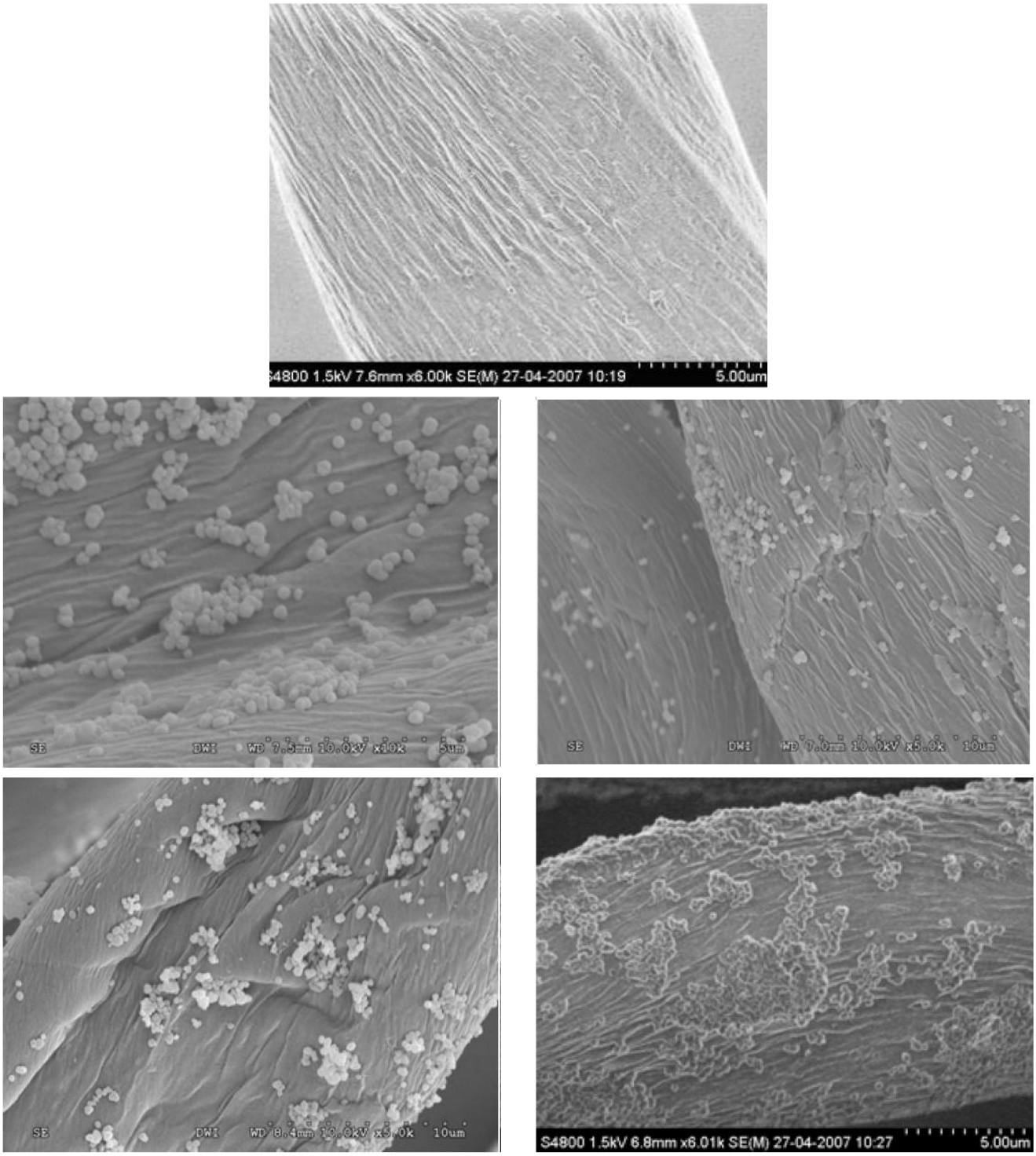


Figure 8: SEM imageof untreatedand treated cotton fibreat different Ph; a) Untreated cotton fibre, b) Treated cotton fibre at pH 3, c) Treated cotton fibre at pH 5, d) Treated cotton fibre at pH 7, e) Treated cotton fibre at pH 9

the charge distribution along the fibres surface is more uniform than in case of wool.

Wool fibre

The SEM images of untreated and treated wool fibres (Figure 9) put into evidence a quite different behaviour from those of cotton.

Firstly, in line with the data about evolution of zeta-potential of wool with pH[23] the pictures show an increase of coating layer with increasing pH-values, after recording almost no particles adhered at pH 3.

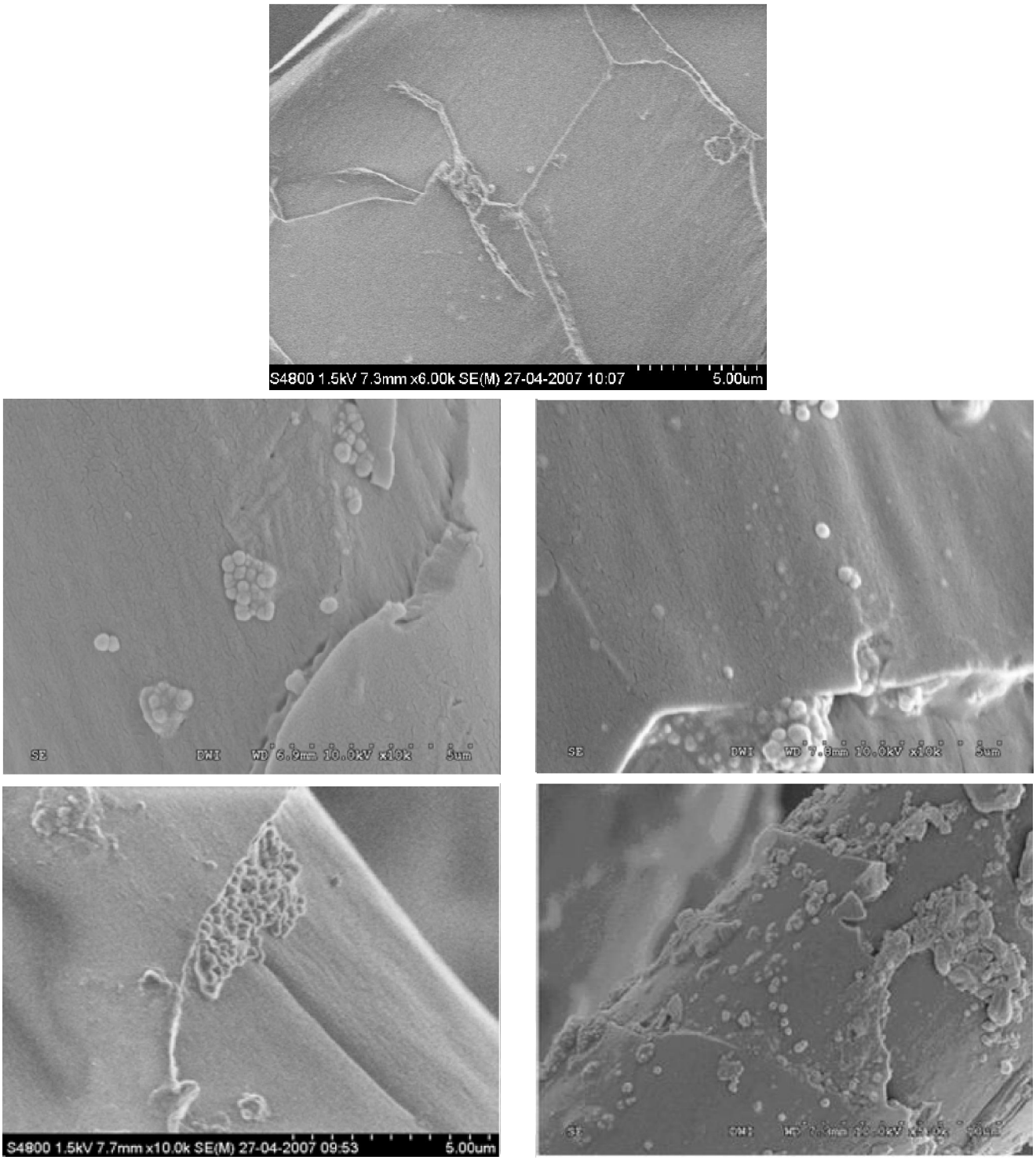


Figure 9 : SEM imageof untreatedand treated wool fibreat different pH; a) Untreated wool fibre, b) Treated wool fibre at pH 3, c) Treated wool fibre at pH 5, d) Treated wool fibre at pH 7, e) Treated wool fibre at pH 9

Secondly, at pH 5 and 7, where the layer is still very scarce, one notices that the particles agglomerate at the edge of the scales. This behaviour is understandable because the density of negative charge is higher at edges than on the surface, and therefore the attraction of positively charged particles is higher at those places. As, generally, the amount of particles attracted by wool fibre is lower than those attracted by cotton fibre, and the wool fibres has the scales on surface as points of surface disruption, the

TABLE 1 : Fluorescencemeasurementsof polymer (5), silica pigments, and a mixture of both

	Polymer 5		Silica pigment		Polymer/Pigment Mixture	
	λ / nm	Intensity	λ / nm	Intensity	λ / nm	Intensity
Emission	468.6	56.085	477.7	79.129	471.5	754.981
Ex 1	387.37	49.76	387	62.92	387.37	103.88
Ex 2	555.71	31.97	570	58.61	498.36	111.93

Spectral rangeof the incident light: 200 - 900 nm

overall aspect of wool coating at pH 5 and 7 is relatively patchy. It is only at pH 9, when the density of charges on wool surface is high enough, that the electric effect of scales reduces and coating layer becomes more uniform, closer to cotton surface.

As a result of these observations wool, although alkaline pH is unsuitable for preserving the keratin structure, is preferable to be coated at pH 9, very much like cotton fibre.

CONCLUSIONS

Synthesis of functional polyethers based on linear polyglycolcidol derivatives was successfully performed, and demonstrated by both NMR as well as GPC analysis. The introducing of the protected groups for hydroxyl groups and their subsequent conversion to quaternized amines and silation via the intermediate stage of a phenyl carbonates was also successfully achieved. We obtained, this way, polymers which fulfil the requirements of having cationic nature, potential of connectivity and partial hydrophobicity.

The polymers were complexed with a selected dye pigment and these complexes were applied at different pH values on fibres of cotton and of wool, respectively. The SEM images of treated fibres indicate that the treatment of both cotton and wool in the range of pH = 7…9lead to the highest coverage. While this range suits cotton also from point of view of its chemical structure, and application can be performed without special requirements, the alkaline pH is relatively dangerous for wool fibres, and, therefore, the treatment has to be carried carefully in terms of low temperature and short time. The conditions we used, of 50 °C and 30 minutes, satisfy these minimal requests and can be considered as optimal for application on keratin fibres.

ACKNOWLEDGEMENTS

Authors are grateful to the DWI an der RWTH Aachen Germany for providing facilities to support this research.

REFERENCES

[1] R.F.Nickerson; 'Cotton fibers constitution, Structure, and Mechanical Properties', *Industrial & Engineering Chemistry*, **32(11)**, 1454-1462 **(1940)**.

[2] K.M.Paralikar, S.M.Betrabet, N.V.Bhat; 'The crystal structure of cotton cellulose investigated by an electron diffraction technique', *Journal of Applied Crystallography*, **12,6**, 589-591 **(1979)**.

[3] V.K.Varshney, S.Naithani; 'Chemical functionalization of cellulose derived from nonconventional sources', in 'Cellulose Fibers: Bio- and Nano-Polymer Composites, Green Chemistry and Technology', (eds.S.Kalia, et al.), **750**, **(2011)**.

[4] M.V.Makarenko, E.V.Gert, F.N.Kaputskii; 'Accessibility of the structure of cotton cellulose modified by nitrogen-oxides in acetic-acid', *Journal Of Applied Chemistry Of The Ussr*, **55,11**, 2298-2302 **(1982)**.

[5] H.Nowotny, H.Zahn; 'The fine structure of wool keratin', *Zeitschr Physikal Chem Abt B,* **51(5),** 265-280 **(1942)**.

[6] M.L.Huggins; 'The structure of fibrous proteins', *Chem Rev*, **32(2)**, 195-218 **(1943)**.

[7] A.R.Lang; 'An X-ray study of alpha-keratin, 1.A General Diffraction Theory for convoluted chain structure and an approximate theory for coiled-coioils', *Acta Crystallographica*, **9,4**, 436-445 **(1956)**.

[8] P.Mason; 'Viscoelasticity and structure of fibrous proteins, 2.Further dynamic measurements of keratin', *Kolloid-Zeitschrift And Zeitschrift Fur Polymere*, **218,1**, 46 **(1967)**.

[9] L.J.Hogg, H.G.M.Edwards, D.W.Farwell,

A.T.Peters; 'Ft raman-spectroscopic studies of wool', *Journal of the Society of Dyers and Colourists*, **110,5-6**, 196-199 **(1994)**.

[10] B.Holmbom; 'Molecular interactions in wood fibre suspensions', *Iswpc - 9th International Symposium On Wood And Pulping Chemistry - Oral Presentations*, PL31-PL36 **(1997)**.

[11] S.Volooj, C.M.Carr, R.Mitchell, J.C.Vickerman; 'Time-of-flight secondary ion mass spectrometry (ToF-SIMS) analysis of the bleaching of keratin fibres and the application of cationic alkyl protein softeners to bleached cashmere', *Surface And Interface Analysis*, **29,7**, 422-430 **(2000)**.

[12] T.Topalovic, V.A.Nierstrasz, L.Bautista, D.Jocic, A.Navarro, M.Warmoeskerken; 'XPS and contact angle study of cotton surface oxidation by catalytic bleaching', *Colloids And Surfaces A-Physicochemical And Engineering Aspects*, **296,1-3**, 76-85 **(2007)**.

[13] P.R.Dvornic, J.Hu, D.J.Meier, R.M.Nowak, N.Parham; *US Patent*, **6**, 534 **(2003)**.

[14] M.Hans, Y.Xiao, H.Keul, A.Heise, M.Moeller; 'Novel biodegradable heterografted polymer brushes prepared via a chemoenzymatic approach', *Macromolecular Chemistry and Physics*, **210,9**, 736-746 **(2009)**.

[15] S.Rangelov, B.Trzebicka, M.Jamroz-Piegza, A.Dworak; 'Hydrodynamic behavior of high molar mass linear polyglycidol in dilute aqueous solution', *Journal of Physical Chemistry B*, **111,38**, 11127-11133 **(2007)**.

[16] P.Dimitrov, S.Rangelov, A.Dworak, N.Haraguchi, A.Hirao, C.B.Tsvetanov; 'Triblock and radial star-block copolymers comprised of poly(ethoxyethyl glycidyl ether), polyglycidol, poly(propylene oxide) and polystyrene obtained by anionic polymerization initiated by Cs initiators', *Macromolecular Symposia*, **215**, 127-139 **(2004)**.

[17] M.Erberich, H.Keul, M.Moller; 'Polyglycidols with two orthogonal protective groups: Preparation, Selective deprotection, and functionalization', *Macromolecules*, **40,9**, 3070-3079 **(2007)**.

[18] A.O.Fitton, J.Hill, D.E.Jane, R.Millar; 'Synthesis of simple oxetanes carrying reactive 2-substituents', *Synthesis*, **12**, 1140-1142 **(1987)**.

[19] M.Erberich; 'Polyglycidole mit selektive adressierbaren schutzgruppen zur darstellung funktionaler polyether', RWTH Aachen, Aachen, **(2006)**.

[20] J.W.Xu, W.F.Shi, W.M.Pang; 'Synthesis and shape memory effects of Si-O-Si cross-linked hybrid polyurethanes', *Polymer*, **47,1**, 457-465 **(2006)**.

[21] W.Ingamells, N.Ramadan; 'The influence of finishing agents on the performance of fibres during electrostatic flocking', *Journal of the Society of Dyers and Colourists*, **108,5-6**, 270-278 **(1992)**.

[22] S.Duquesne, C.Magniez, G.Camino; Eds.: *Multifunctional Barriers for Flexible Structure: Textile, Leather and Paper*, (ed.R.Hull, et al.), Heidelberg, Springer-Verlag, **(2007)**.

[23] T.Luxbacher; 'Electrokinetic properties of natural fibres', in 'Handbook of Natural Fibres', (ed.R.Kozlowski), Cambridge UK, Woodhead Publishing Ltd, **(2012)**.