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Hydrolysis and Subsequent Quaternization of Poly[(Isobutene-*co*-(m,p)-chloromethylstyrene)-*g*-2-methyl-2-oxazoline] and Poly((m,p)-Chloromethylstyrene-*g*-2-methyl-2-oxazoline)

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HYDROLYSIS AND SUBSEQUENT QUATERNIZATION OF POLY[(ISOBUTENE-*CO*-(M,P)-CHLOROMETHYLSTYRENE)-*G*-2-METHYL-2-OXAZOLINE] AND POLY((M,P)-CHLOROMETHYLSTYRENE-*G*-2-METHYL-2-OXAZOLINE)

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ABSTRACT

The graft copolymers poly[(isobutene-*co*-(m,p)-chloromethylstyrene)-*g*-ethyleneimine)] **HPG1** and poly((m,p)-chloromethylstyrene-*g*-ethyleneimine) **HPG2** were obtained through the alkaline hydrolysis of the amphiphilic graft copolymers poly[(isobutene-*co*-(m,p)-chloromethylstyrene)-*g*-2-methyl-2-oxazoline] and poly((m,p)chloromethylstyrene-*g*-2-methyl-2-oxazoline), respectively. The subsequent quaternization of **HPG1** and **HPG2** with methyl iodide resulted in new polyelectrolyte graft copolymers which are soluble in water despite of the hydrophobic backbone.

INTRODUCTION

Commercial poly(ethyleneimine), obtained through the cationic polymerization of aziridine, is a branched polymer of amorphous character and soluble in water at room temperature[1]. In contrast to this the linear poly(ethyleneimine) which is obtained via hydrolysis of poly(2-alkyl(aryl)-2-oxazoline) is a highly crystalline polymer insoluble in cold water but soluble in hot water[1]. Linear poly(ethyleneimine) can be utilized e.g. for the synthesis of multifunctional catalysts or enzyme models; in general, alkyleneimine polymers have a very broad application spectrum e.g. in biomedicine and in textile and paper industry[1,2]. Besides the poly(ethyleneimine) homopolymers, statistical, block and graft copolymers with ethyleneimine units are of interest due to special solubility, viscosity and chelating properties[1]. Graft copolymers with polyethyleneimine graft arms and polystyrene backbone have been synthesized via the macromonomer route[3] as well as via "grafting onto"[4] and "grafting from"[5]. In the latter the macroinitiator was obtained from polystyrene and subsequent partial chloromethylation of the aromatic unit. The resulting chloromethylstyrene units functioned as initiating sites for the ring opening polymerization of 2-methyl-2-oxazoline[5]. Recently we reported the cationic copolymerization of isobutene and (m,p)-chloromethylstyrene and the use of these copolymers as macroinitiators for the polymerization of 2-methyl-2-oxazoline. Highly amphiphilic graft copolymers were obtained by this method[6]. Now we would like to present our results on the hydrolysis and subsequent quaternization of these graft copolymers.

EXPERIMENTAL PART

Materials

Chloromethylstyrene CMS (mixture of 70% *meta*- and 30% *para*-substituted isomers) was distilled twice under vacuum and stored under dry nitrogen. Benzonitrile and 2-methyl-2-oxazoline (MeOXA) from Aldrich were bidistilled over CaH_2 and stored under dry nitrogen. Isobutene (Linde), of 99,96% purity, was dried over molecular sieves (4Å) and potassium on Al_2O_3. BCl_3, CH_3I, sodiumhydroxid, $AgNO_3$ and 2,2-azobis(isobutyronitrile) (AIBN) were obtained from Aldrich and were used as received. 1,2,2,6,6-Pentamethylpiperidine (PMP) was synthetized according to a method described in the literature[7]. Linear poly(2-ethyl-2-oxazoline) of $\overline{M}_w$ = 50000 g/mol was obtained from Aldrich. CH_3OH was destilled before use. The synthesis of the poly(isobutene-*co*-chloromethylstyrene) **MI1** with 58 mol% CMS and a molar mass $\overline{M}_n$ = 7400 has been described previously[6]. Linear poly((m,p)-chloromethylstyrene) **MI2** ($\overline{M}_n$ = 21200 g/mol, $\overline{M}_w/\overline{M}_n$ =2.87) was synthesized via free radical polymerization using AIBN as initiator according to the literature[8].

Instruments

NMR spectra were taken with a Bruker ARX 300 (resonance frequencies: 300 MHz for ^1H and 75.5 MHz for ^{13}C). A Bruker IFS 55 was used for the FT-IR measurements in KBr and chloroform solution. The UV/VIS spectra were taken with a Varian Cary 3. A Waters system (pump 510, UV detector 486, RI detector 410, ultrastyragel 7 µm columns (500, 10^3, 10^4, 10^5)) with THF as eluent at a flow rate of 0.5 mL/min and calibrated with polystyrene standards was applied for GPC measurements. Elemental analyses were carried out in the laboratories of organic and inorganic chemistry of the Technical University Munich. Solution viscosity measurements were carried out at 25°C in methanol utilizing Ubbelohde viscosimeter from Schott and a MGW-Lauda Thermostate D60S.

*Synthesis of Graft Copolymers **GP1** and **GP2***

The synthesis of poly[(isobutene-*co*-(m,p)-chloromethylstyrene)-*g*-2-methyl-2-oxazoline] **GP1** from **MI1** has been described before[6]. A graft copolymer with a wt. ratio backbone/poly(MeOXA) graft arms of 2/40.5 and an average degree of polymerization $\overline{P}_n$ of the graft arms of 46 was used in the following experiments. The synthesis of poly((m,p)chloromethylstyrene-*g*-2-methyl-2-oxazoline) **GP2** from **MI2** was carried out similarly as described for **GP1**[6] in benzonitrile at 110 °C for 48 hrs. with a conversion of MeOXA = 53%. The wt. ratio backbone/graft arms in **GP2** was 2/37.5 and from this the $\overline{P}_n$ of the graft arms was calculated to be 34 assuming that all initiator functions were active.

*Hydrolysis of Graft Copolymers **GP1** and **GP2***

The general procedure described by Saegusa et al.[9] for the alkaline hydrolysis of poly(2-methyl-2-oxazoline) was followed (compare Table I). Typical example (**HGP1**): 8.0 g. (0.0896 mol N-acetyl-ethyleneimine content) of **GP1** were refluxed for 65 hours with 10.0 g (0.25 mol) of sodium hydroxide in 140 mL water. Upon cooling, the precipitate formed was removed by filtration and washed until the washings became neutral. Three recrystallizations in hot water were carried out. Final drying under vacuum at 40 °C gave 4.7 g of the product. Bound water was removed by evacuating the product to 1 mm Hg at 65-70°C for 2 h. On cooling, a hard, hygroscopic, semitransparent graft copolymer with anhydrous poly(ethyleneimine) side chains was obtained in 85% yield. Mp 59-60°C (58,5°C in the literature[1]) for linear homo-poly(ethyleneimine)).

IR (KBr) in cm^{-1}: 3420, 2820, 1640, 1458, 1140

^1H NMR ($CDCl_3$), δ in ppm: poly(isobutene) peaks (weak): 1.1 (s, CH_3), 1.4 (s, CH_2); poly(ethyleneimine) peaks: 2.0 (s, b, NH), 2.7 (s, b, CH_2); CMS units (weak): 6.5 -7.5 (b, ar)

^{13}C NMR ($CDCl_3$), δ in ppm: 49.4 (CH_2, poly(ethyleneimine); 31.7, 38.0, 60.5 (CH_3, C, CH_2, isobutene units), 41.7, 52.2, 54.9, 59.4 (CH_2, CH, CMS units)

Quaternization Procedure

The method developed by Sommer et. al.[7] for the synthesis of quaternary ammoniun compounds was used (compare Table II). Typical example (**QGP2**): A solution of 0.2 g (4.24 mmol ethyleneimine content) of **HGP2**, 0.66 g (4.25 mmol) of 1,2,2,6,6-pentamethyl piperidine (PMP), and 6.8 g (48 mmol) of methyl iodide in 15 mL methanol was kept overnight at room temperature. The hard and transparent solid that formed was removed by filtration and washed with a solution of

TABLE I
Reaction conditions and results of the hydrolysis of graft copolymers **GP1** and **GP2** (at 100 °C)

HGP	from	amount GP in g	[NaOH]/ [N-acetyl][1]	water in mL	time[2] in h	hydrolysis[3] in %	yield in g
HGP1	**GP1**	8.0	2.5	140	65	100	3.6
HGP2	**GP2**	10.0	2.5	150	65	100	3.7
HGP3	**GP1**	4.0	0.75	50	120	75	1.8
HGP4	**GP2**	4.0	0.75	50	120	75	1.7

[1] initial molar ratio of NaOH to N-acetyl groups in the graft copolymer
[2] hydrolysis reaction time
[3] degree of hydrolysis in **HGP** determined from ^{1}H NMR spectroscopy

TABLE II
Reaction conditions and results of the quaternization of **HGP1** and **HGP2** (at 25 °C, 0.7g PMP[1])

QGP	from	amount HGP in g	amount CH_3I in g	MeOH in mL	yield in g	quaterniza-tion[2] in %	iodine con-tent[3] in %
QGP1	**HGP1**	0.20	6.8	15	0.42	70	56.5
QGP2	**HGP2**	0.20	6.8	15	0.62	64	54.1
QGP3	**PEI**[4]	0.20	6.8	15	0.32	60	56.0

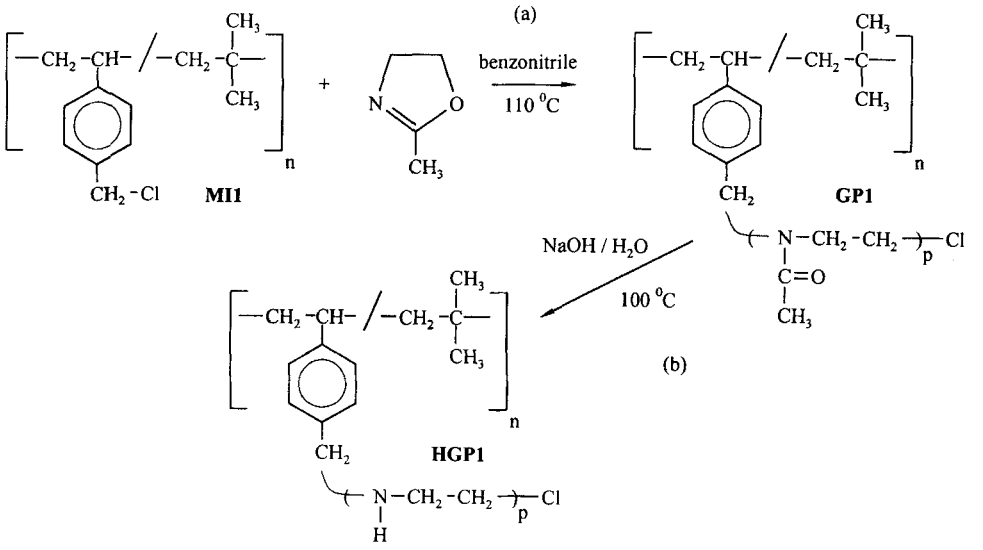
[1] PMP = 1,2,2,6,6,-pentamethyl piperidine. All reactions were carried out overnight
[2] quaternization degree in %; determined from the iodine content in **QGP**
[3] iodine content in the quaternized graft copolymers (from elemental analysis)
[4] **PEI** = linear poly(ethyleneimine) (96.5 % hydrolyzed), obtained via hydrolysis of poly(2-ethyl-2-oxazoline) ($\bar{M}_w$ = 50000 g/mol)

N,N-dimethylformamide in acetone (6% v/v) to give 0.62 g of the quaternized polymer as pale yellow solid with a crystalline character. The test reaction of the quaternized polymer with silver nitrate was positive giving a yellow-green silver iodide precipitate. The quaternization degree was determined from the iodine analysis to be 64% (compare Table II).
^{1}H NMR (D_2O), δ in ppm: 2.9 (s), 3.3 - 4.3 (m), 4.4 - 5.3 (m) (N-CH_2 and N-CH_3) ; poly(isobutene-*co*-CMS) signals not detectable;
Elemental analysis (**QGP2**, 64 mol% quaternized):

calculated	C	28.8	H	5.7	N	9.4	I 55.3
found	C	27.2	H	6.0	N	8.1	I 54.1

RESULTS AND DISCUSSION

Two different graft copolymers **GP1** and **GP2** prepared from the macroinitiators **MI1** and **MI2** and 2-methyl-2-oxazoline (MeOXA) were used for the experiments described here. The synthesis of **GP1** with a slightly branched copolymer **MI1** of isobutene and chloromethylstyrene (poly(PIB-*co*-CMS) as backbone has been described previously[6] (Scheme 1, (a)). In an analogous procedure, linear homo-poly((m,p)-chloromethylstyrene) **MI2** obtained from free radical polymerization[8] was grafted with MeOXA to form **GP2**.



Scheme 1

The macroinitiators **MI1** and **MI2** were obtained with an $\overline{M}_n$ of 7400 and 21200 g/mol, respectively, and **MI1** with a CMS content of 58 mol%. The ring-opening cationic polymerization of 2-methyl-2-oxazoline using these macroinitiators yielded water soluble graft copolymers with an approximate wt-ratio backbone to graft arms of 2/39 and a calculated average degree of polymerization $\overline{P}_n$ for the graft arms of 46 (**GP1**) and 34 (**GP2**) assuming 100% initiator efficiency.

The alkaline hydrolysis of the graft copolymers **GP1** and **GP2** was carried out over 65 h using an aqueous solution of NaOH according to the method described by Saegusa et al.[9] for the hydrolysis of poly(2-methyl-2-oxazoline) (Scheme 1, (b)). The reaction conditions and results are summarized in Table I. In contrast to the hydrolysis of homo-poly(2-methyl-2-oxazoline) during which a rapid precipitation of the partially hydrolyzed polymer takes place[9], the reaction medium in the hydrolysis reaction of **GP1** and **GP2** remained homogenous for 40 hrs, and only then a gradual precipitation of the hydrolyzed graft copolymer was observed. This phenomenon is probably due to the amphiphilic character of the graft copolymer.

The degree of hydrolysis was calculated from the ^{1}H-NMR spectrum using the integral ratio of the methylene protons adjacent to secondary amino groups and those adjacent to the N-acetyl group. A 100% hydrolysis of **GP1** and **GP2** after 65 hours was achieved (**HGP1, HGP2**) with the initial molar ratio [NaOH] /[N-acetyl] = 2.5 and the absolute NaOH concentration = 2.0 mol/L, as indicated by the complete disappearance of the ^{1}H NMR signals for the N-acetyl groups (2.1 ppm), the appearance of the NH-signal at 2.0 ppm, and the shift of the signals for the methylene protons from 3.5 to 2.7 ppm. Due to the large weight excess of the graft arms the signals for the backbone at 1.1 and 1.4 (PIB) and in the aromatic range (6.5 - 7.5) are very weak (Fig.1). Only 75% hydrolysis was obtained when the molar ratio [NaOH]/[N-acetyl] was dropped to 0.75 (Table I, **HGP3, HGP4**), thus the degree of hydrolysis can be controlled by the stoichiometry as already described in the literature for homo-poly(N-acetylethyleneimine)[1].

The ^{13}C-NMR spectra of **HGP1** and **HPG2** exhibit only a single strong peak at 49.4 ppm, corresponding to the methylenic carbons of the secondary amine, and several very weak peaks for

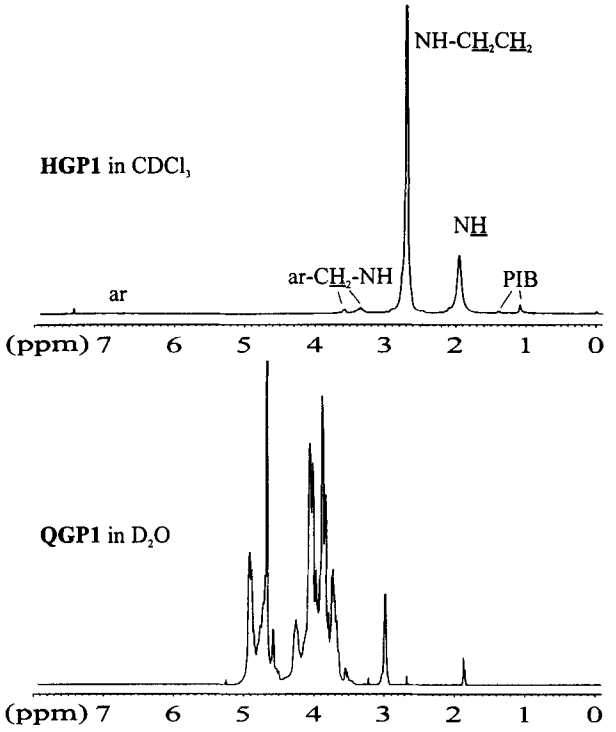
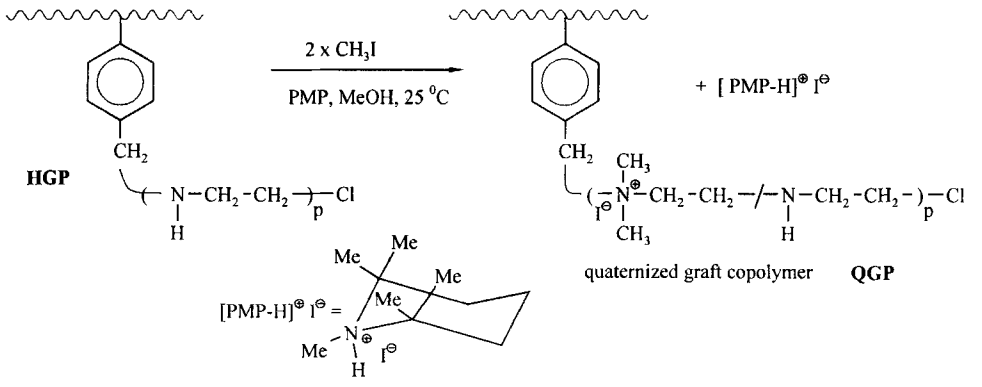


Fig. 1: ^{1}H NMR spectra of **HGP1** and **QGP1** in $CDCl_3$ and D_2O, respectively (PIB = signals of the isobutene units in the backbone; ar and ar-CH_2-NH = signals of the CMS units of the backbone).

the backbone (30 to 60 ppm). This proves, as expected, that the graft copolymers have linear poly(ethyleneimine) graft arms since branched poly(ethyleneimine) exhibits 8 peaks for the methylenic carbons in the ^{13}C spectrum[10]. The linearity of the graft arms is also demonstrated by the fact that a melting point can be observed for **HGP1** and **HPG2** at 59-60 °C which is very close to that observed for linear homo-poly(ethyleneimine)[1] **PEI** and the polymer is soluble only in hot water, chloroform and methanol.

The UV spectra in methanol of **HGP1** and **HGP2** show clearly that the absorption of the N-acetylethyleneimine units at 300 nm disappeared after hydrolysis. However, the absorption of the aromatic units in the backbone at 230 nm remained. In the IR spectra of **HGP1** and **HGP2** in chloroform solution the typical carbonyl absorption ($\nu_{c=o}$ = 1650 cm^{-1}) of the amide function has disappeared completely after hydrolysis.

The hydrolyzed graft copolymers **HGP1** and **HGP2** were submitted to a quaternization reaction using methyl iodide in methanol at 25°C (Scheme 2) as employed by Sommer et al.[7]. The reaction conditions and results are sumarized in Table II. The method utilizes the fact that the protonation of sterically hindered amines is affected only slightly by steric hindrance, whereas their nucleophilicity as measured by the rate of alkylation is considerably decreased. A sterically hindered organic base of greater base strength than the reactant amine is employed to bind the acid that is generated in the alkylation reaction. In our case, the sterically hindered organic base was 1,2,2,6,6-pentamethyl piperidine (PMP) of a pK_a = 11.25. PMP is readily protonated, however, it is a relatively poor



Scheme 2

The quaternization degree was determined from iodine elemental analysis assuming the idealized average structure for the quaternized graft copolymer **QGP** as given in Scheme 2. As a result of the quaternization reaction a new type of polyelectrolyte graft copolymers with polar quaternized poly(ethyleneimine) graft arms and a hydrophobic backbone was obtained. The polymers are brittle, transparent, crystallin and soluble in water in low concentrations at room temperature an in higher concentrations at 70 °C. The quaternization degree of **QGP1** (based on **HGP1**) was 70 % and of **QGP2** (based on **HGP2**) 64 % (Table II) with a higher product yield of **QGP2**. Similarly, the quaternization degree of linear poly(ethyleneimine) **PEI**, obtained via acid hydrolysis of poly(2-ethyl-2-oxazoline) (96.5 % hydrolyzed), was 60 %, however, the product yield was very low under equal reaction conditions. The reference experiment in the absence of a poly(ethyleneimine) polymer proved that no quaternization of 1,2,2,6,6-pentamethyl piperidine takes place under these conditions. The ^{1}H NMR spectra in D_2O of the hydrolyzed products **QGP** exhibit multiplets for the quaternized poly(ethyleneimine) graft arms (Fig.1) and the signals of the backbone are not detectable due to the shielding of the unpolar backbone by the very polar graft arms as observed similarly for the original graft copolymers **GP**[6].

We carried out viscosity measurements on methanol solutions of the hydrolyzed polymers **HGP1** and **HGP2**, the original graft copolymers **GP1** and **GP2**, and the linear poly(ethyleneimine) **PEI**. In Fig.2 the reduced viscosities η_i/c are plotted versus the concentration. The graft copolymers **GP** show relatively little dependence of the reduced viscosity on the concentration despite of their high molar mass because these polymers have the tendency to form aggregates in aqueous, methanol and chloroform solutions, as already was demonstrated and discussed in the previous paper[6]. However, the reduced viscosity is dependent on the molar mass: η_i/c of **GP2** is almost twice that of **GP1**. Assuming an ideal grafting reaction, a molar mass $\overline{M}_n$ of approximately 150000 g/mol and 400000 g/mol can be estimated for **GP1** and **GP2**, respectively, based solely on the weight ratio backbone/graft arms since direct analysis of the molar masses was not possible. The hydrolyzed graft copolymers **HGP** exhibit a higher reduced viscosity than their corresponding graft copolymers **GP** but still with no dependency on the concentration. In strong contrast to this, the linear **PEI** (M_w of the starting polymer = 50000 g/mol) exhibits the highest reduced viscosity and a dependence of η_i/c on the concentration. These results demonstrate very impressively the large influence of the spatial arrangement of graft arms on a hydrophobic backbone on the viscosity behavior even though the weight content of the backbone in the graft copolymers is extremely low. A logical conclusion would

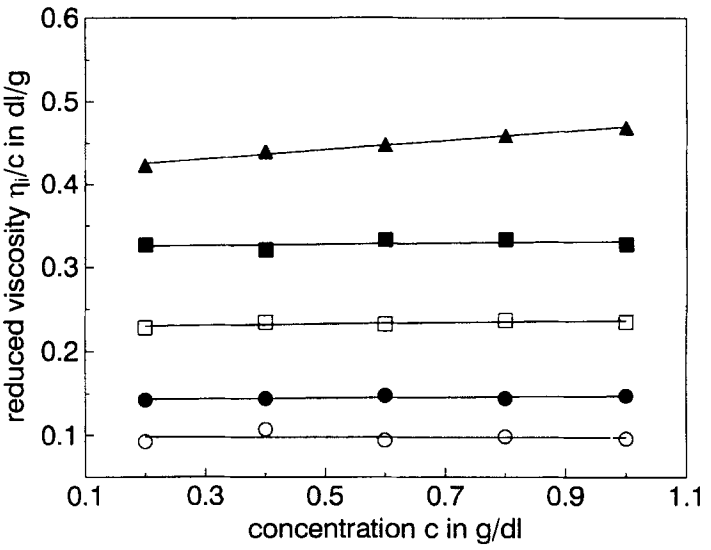


Fig. 2: Reduced viscosities η_i/c versus concentration plot for **GP1** (○) and **HGP1** (●), **GP2** (□) and **HGP2** (■), and for **PEI** (▲), measured in methanol at 25 °C.

be that the graft copolymers **GP** as well as the hydrolyzed products **HGP** exhibit in solution a structure which resembles a star architecture with the hydrophobic backbone collapsed as core.

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