Synthesis of Double Hydrophilic Graft Copolymers with a Polyacetal Backbone

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ABSTRACT: Cationic copolymerization of a functional aldehyde, methyl glyoxylate (GM), with a seven-membered cyclic acetal, 1,3-dioxepane (DXP), leads to polyacetals containing ester side groups that may be used for functionalization. Partial replacement of the ester groups in GM−DXP copolymers with amide groups by reaction with α-amino-ω-methoxypoly(oxyethylene) (Jeffamine) led to graft copolymers, and the remaining ester groups could easily be hydrolyzed to carboxylate groups. The resulting water-soluble graft copolymers, containing poly(oxyethylene) side chains and carboxylate groups along the main chain, belong to the class of double hydrophilic copolymers that are recently studied as modifiers of the processes occurring at the interface between crystal surfaces and surrounding solution.

Introduction

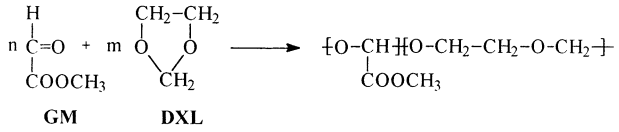
We have recently reported on the synthesis of polyacetals containing functional groups that may be used for further modification.[1] Functionalized polyacetals were prepared by the cationic copolymerization of methyl glyoxylate (GM—an aldehyde containing an ester group studied earlier by Vairon et al.[2,3]) with 1,3-dioxolane (DXL—five-membered cyclic acetal); see Scheme 1. Copolymers with M_n up to 2×10^4 containing from 10 to 70 mol % of GM repeating units were obtained.

Polyacetals undergo degradation under acidic conditions (thus they may be considered to be degradable polymers) but are stable under basic conditions.[4] Therefore, under basic conditions, the ester side groups of those copolymers may be converted into other functional groups without affecting the main chain. One possible reaction that may be envisaged is a basic hydrolysis of ester groups to carboxylate groups leading to polyacetals containing ionic side groups along the main chain. Ester or carboxylate groups may be also used to attach other polymer chains as side chains, leading to graft copolymers. If the side chains were made of poly(oxyethylene), the resulting graft copolymers would contain ionic side groups along the main chain and hydrophilic side chains; two features which are required for so-called double hydrophilic copolymers that have been recently extensively studied as modifiers of crystallization and mineralization processes.[5]

The synthetic usefulness of the described system (copolymerization of GM with DXL) is, however, limited. In this system, relatively large amounts of low molar mass cyclic oligomers are formed decreasing the yield of linear copolymer. The cyclic fraction contains predominantly mixed cyclic dimer (MCD) composed of one GM and one DXL unit. The content of MCD varies between 15 and 70 wt % depending on the composition of the feed.

Extensive cyclization is due to the low ring strain in MCD being a seven-membered ring. It was shown that formation of MCD is a reversible process; thus, MCD formed can be incorporated back into the chain.[1] Its equilibrium concentration is, however, relatively high, and that leads to high content of MCD in the final product.

Scheme 1



GM DXL

To devise a system in which copolymerization of GM with a cyclic acetal would lead to a functional linear polyacetal essentially free of cyclic fraction, in the present paper, we report on the cationic copolymerization of GM with a seven-membered cyclic acetal: 1,3-dioxepane (DXP). The corresponding mixed cyclic dimer (if formed) would be a nine-membered ring. Because of the higher ring strain of a nine-membered ring as compared to a seven-membered one (GM−DXL dimer), its equilibrium concentration should be much lower, resulting in a higher yield of linear copolymer and opening thus a synthetic pathway for feasible synthesis of double hydrophilic graft copolymers by further transformation of functional groups along the polyacetal chain.

Experimental Section

Materials. Methyl glyoxylate (GM) (kindly provided by former Société Française Hoechst, now Clariant) is a mixture of oligomers in form of a viscous liquid (GM undergoes spontaneous polymerization upon storage). Monomeric GM was obtained by depolymerization proceeding in the course of vacuum distillation over P_2O_5. The fraction boiling at 44 °C (45 mbar) was collected and used for copolymerization. GM was stored in a closed ampule under vacuum at −5 °C.

1,3-Dioxepane (DXP) was synthesized from butylene glycol and formaldehyde.[6] It was purified by refluxing over CaH_2 followed by distillation (bp = 119 °C) to an ampule over a sodium mirror. It was subsequently condensed in a container on the vacuum line and stored in a closed ampule under vacuum over sodium−potassium alloy.

Trifluoromethanesulfonic acid (triflic acid, TfOH) (Aldrich) was purified by distillation (bp = 162 °C) and distributed into phials sealed under vacuum.

Methylene chloride (CH_2Cl_2) was washed with concentrated sulfuric acid to remove unsaturated impurities. This procedure was repeated until the acid layer remained colorless. CH_2Cl_2 was subsequently washed with water, 5 wt % aqueous $NaHCO_3$, and again with distilled water. After preliminary

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drying with $CaCl_2$ for 24 h, it was refluxed over CaH_2 for 6 h and distilled. The fraction boiling at 39−40 °C was collected in an ampule containing fresh CaH_2. Finally CH_2Cl_2 was condensed on a vacuum line into an ampule over a sodium mirror.

α-Amino-ω-methoxypoly(oxyethylene) (Jeffamine-560) (Texaco Chemical Company, USA) was dried for 8 h on the vacuum line prior to use.

Copolymerization of GM with DXP. Copolymerization was carried out in ampules sealed under vacuum. The typical experimental procedure is described below. The phial containing TfOH initiator (0.0089 g, 5.93×10^{-5} mol) was placed together with a glass-covered iron bar (allowing breaking of a vial with a magnet) inside an ampule equipped with a Rotaflo stopcock. After the ampule was connected to the vacuum line, the required amounts of GM (1.20 g, 1.36×10^{-2} mol), DXP (2.7 g, 2.65×10^{-2} mol), and CH_2Cl_2 (6.1 mL) were distilled into the ampule. The ampule was placed in a cooling bath, and the phial containing the initiator was broken to start the reaction. Copolymerization was terminated by addition of a 5-fold excess (with respect to acid) of CH_3ONa dissolved in CH_3OH (approximately 5 wt % solution). Copolymers were isolated by evaporation of solvent using a rotary evaporator.

Synthesis of Graft Copolymers (Reaction of GM—DXP Copolymers with Jeffamine. A typical experimental procedure is described below. First, 2.28 g of GM−DXP copolymer (M_n = 4400, [GM]/[DXP] = 0.46/0.54) and 4.99 g (8.96×10^{-3} mol, which corresponds to 80 mol % with respect to $COOCH_3$ groups) of Jeffamine-560 (M_n = 560 according to manufacturer specification) were placed in a flask and connected to the vacuum line. The contents of the flask were magnetically stirred and heated at 50 °C. Volatile products (CH_3OH) were condensed in a trap cooled with liquid nitrogen. After 6 h, the content of the flask was dissolved in 6 mL of CH_2Cl_2. Unreacted Jeffamine was extracted with water (three portions of about 15 mL each). After evaporation of solvent from the organic phase using a rotary evaporator, 4.82 g of graft copolymer was obtained. SEC analysis confirmed nearly quantitative removal of unreacted Jeffamine.

Hydrolysis of the Remaining Ester Groups in Graft Copolymers. First, 4.82 g of graft copolymer was dissolved in 20 mL of CH_3CN, and two drops of phenolphthalein indicator was added. The contents of the flask were magnetically stirred, and 4 wt % aqueous KOH was added dropwise until a persistent violet color indicated that hydrolysis was complete. Hydrolyzed graft copolymers were purified by ultrafiltration using a membrane with a cutoff at molar mass = 500. The complete disappearance of the signal of $COOCH_3$ group (δ = 3.82 ppm) in ^{1}H NMR spectra of copolymer after hydrolysis confirmed that the hydrolysis was quantitative.

Measurements. NMR spectra were recorded with a Bruker AC 200 instrument (200 MHz for ^{1}H and 50.33 MHz for ^{13}C NMR) with proton decoupling for ^{13}C NMR spectra.

SEC analysis was performed using a LKPB-2150 instrument equipped with Waters TSK G 4000HXL and G2000HXL columns and an RI−UV detector. CH_2Cl_2 was used as eluent. M_n values were calculated on the basis of polystyrene calibration.

Triple detection SEC analysis (SEC^3) was performed with a Viscotek instrument equipped with triple detector (refractive index, viscosimetry, and right angle laser light scattering) using TSK G4000HXL and G2000HXL columns and CH_2Cl_2 as eluent. The data were processed using TRISEC software.

IR spectra of copolymers (films on KBr pellets) were recorded with an ATI Mattson Infinity Series 60 AR FTIR instrument.

ζ (zeta) potential was measured by electrophoretic light scattering (ELS) technique using the Brookhaven ZetaPlus apparatus.

Results and Discussion

Cationic Copolymerization of Methyl Glyoxylate with 1,3-Dioxepane. Cationic copolymerization of GM with DXP was carried out in methylene chloride as a solvent at −30 °C with trifluoromethanesulfonic (triflic) acid (TfOH) as an initiator. Within the range of concentrations $[GM]_0$ = 1.0−4.7 mol/L, $[DXP]_0$ = 1.2−3.5 mol/L, and $[TfOH]_0 = 5-6 \times 10^{-3}$ mol/L, practically complete conversions of both comonomers (according to ^{1}H NMR) were observed in about 10 min. SEC analysis of the resulting copolymers indicates that M_n depends strongly on the composition of comonomer feed (Table 1).

Table 1. Dependence of M_n of GM−DXP Copolymers on the Composition of Comonomer Feed (Copolymerization Conditions: CH_2Cl_2, −30 °C)

$[GM]_0$, mol/L	$[DXP]_0$, mol/L	$[TfOH]_0 \times 10^3$, mol/L	M_n(SEC)[a]	M_n(SEC)/ M_n(calcd)[b]
2.8	1.2	6.2	900	0.02
2.0	2.0	5.8	4400	0.07
1.3	2.4	5.0	9000	0.13
1.0	3.5	6.0	18 000	0.40

[a] M_n of the crude copolymer obtained by evaporation of solvent calculated using polystyrene calibration. [b] Calculated as for a process without transfer or termination.

For a purified sample of GM−DXP copolymer, molecular weights calculated using SEC with polystyrene calibration (M_n = 4730, M_w = 6270) were very close to those obtained using triple detection SEC (M_n = 4620, M_w = 5570) and not much different from the values determined by tonometry (VPO) (M_n = 5940). It may be concluded therefore that simple SEC using polystyrene calibration gives reasonably good estimation of molecular weights of GM−DXP copolymers.

In the previously studied copolymerization of GM with DXL, a mixed cyclic dimer appeared on the SEC curve as a separate maximum at low molar mass region. In the copolymerization of GM with DXP, although there is a small tail on the SEC curve in the lower molar mass region, no separate peak is observed indicating that low molar mass cyclic oligomers (cyclic dimers) are not formed in measurable quantities. If cyclic dimer were present (molar mass = 190) its signal should appear at the elution volume of 18.8 mL. The difference between both systems is due to the difference in the ring strain of both dimers.

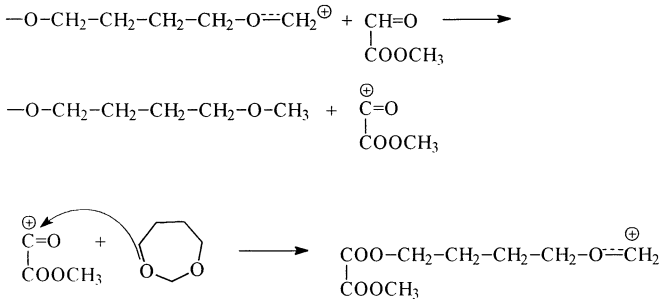
Molar masses of copolymers are considerably lower than calculated for the process without transfer. The dependence of molar masses on the composition of comonomer feed is similar to that observed for the previously studied copolymerization of GM with DXL, namely the lower the fraction of GM in the feed, the higher the M_n value.[1]

Since the essential features of cationic homo- and copolymerization of these two related cyclic acetals are very similar[7] this result indicates that like in GM−DXL system[1] there is an important chain transfer reaction involving hydride transfer from GM molecule to the $-DXP^+$ active center (Scheme 2).

Such a process should lead to formation of methoxy and oxalate end groups. Signals corresponding to these groups were indeed observed in ^{1}H NMR spectra of copolymers at δ = 3.4 ppm (methoxy group) and δ = 4.1−4.3 ppm (oxalate groups).

Analysis of the ^{13}C and ^{1}H NMR spectra allows the determination of the microstructure of GM−DXP copolymers. In ^{13}C NMR spectra, signals of acetal carbons partly overlap. On the other hand, in ^{1}H NMR spectra, signals of protons of acetal groups are separated. Therefore, the conclusions concerning copolymer microstructure were based on analysis of ^{1}H NMR spectra.

Scheme 2



(only carboxonium ion active species being in equilibrium with corresponding oxonium ion are shown for simplicity)

Table 2. Relative Abundance of DXP−DXP Homodiads Calculated on the Basis of Bernoullian Statistics and Determined from ^{1}H NMR Spectra

mol fract of [DXP] units in copolymer (^{1}H NMR)	[DXP−DXP]/([DXP−DXP] + [DXP−GM]) calcd on the basis of Bernoullian statistics	[DXP−DXP]/([DXP−DXP] + [DXP−GM]) determined from ^{1}H NMR spectra
0.36	0.36	0.11
0.55	0.55	0.25
0.67	0.67	0.53
0.72	0.72	0.53

Spectra of copolymers obtained at different feed composition are shown in Figure 1.

The assignments of signals were based on the analysis of spectra of copolymers with varying fractions of both repeating units and analysis of 2D ^{13}C−^{1}H NMR correlation spectra. The spectrum in the region of absorption of protons of the acetal (−OCH_2O− and −OCHRO−) groups is quite complex due to the different regio- and stereosequences possible (GM unit contains a chiral center, leading to additional splitting).

Splitting of the signals of acetal protons is due to the different regio- and stereosequences. The complex character of the spectrum is due mainly to the fact that both monomers contribute different number of atoms to the chain (DXP contributes seven atoms while GM two atoms). Thus, in contrast to the typically encountered situation (e.g., in copolymerization of vinyl monomers), when both comonomers contribute two atoms to the chain and only odd or only even sequences are observed for the particular group,[8] in the system under discussion, both odd and even sequences affect the spectra.

Therefore, we did not attempt to fully analyze the spectra shown in Figure 1, limiting ourselves to rather crude analysis of splitting of acetal protons of the DXP unit. The well separated signal at $\delta = 4.65$ ppm was assigned to protons of the −OCH_2O− group in the DXP−DXP homodiad (the corresponding chemical shift in homopolymer of DXP is equal to 4.74 ppm) while poorly resolved series of signals in $\delta = 4.70-5.00$ ppm region were assigned to various sequences resulting from DXP−GM heterodiad. The integration allowed therefore determination of the relative abundance of DXP−DXP and DXP−GM sequences.

The relative abundance of DXP−DXP homodiads determined from ^{1}H NMR spectra was compared with that calculated for Bernoullian statistics for random distribution of comonomer units. Results are given in Table 2.

The fraction of DXP−DXP homodiads in copolymer is in all instances lower than that calculated for random copolymer, meaning that there is a marked tendency for alternation.

It is well-known that in the cationic copolymerization of cyclic acetals, random copolymers are formed regardless of the ratio between homo- and cross-propagation rate constants.[9] In an attempted synthesis of block copolymers, when DXP was added to a solution of living poly-DXL or vice versa and the polymerization was terminated even before complete (equilibrium) conversion of the second monomer, the product was essentially a random copolymer.[10] This was explained by fast transacetalization (segmental exchange, scrambling) proceeding with a rate comparable to that of propagation. Therefore, even if the kinetics favored formation of longer blocks, transacetalization proceeding parallel to propagation would lead to fast randomization. The tendency for alternation observed in the studied system is apparently due to the steric repulsion between two bulky substituents in GM−GM homodiads.

Synthesis of the Graft Copolymer Containing Polyacetal (GM−DXP Copolymer) Main Chain and Poly(oxyethylene) (POE) Side Chains. The straightforward route to graft copolymers containing a functionalized polyacetal main chain and poly(oxyethylene) (POE) side chains would seem to be the copolymerization of GM with POE macromonomer containing a polymerizable heterocyclic group at one chain end. Unfortunately, all our attempts to copolymerize cationically GM with the macromonomer: POE glicydyl ether failed. Also the copolymerization of GM with DXP was effectively prohibited in the presence of POE macromonomer. This is probably due to the relatively high nucleophilicity of ether oxygen atoms in POE chains as compared to acetal oxygen atoms. Active species of copolymerization are therefore trapped by ether oxygen atoms in the form of the dormant oxonium ions.

To obtain the desired graft copolymers, we therefore applied a two-step procedure. Copolymers of GM with DXP were obtained as described in the previous section and, in the second step, POE side chains were attached through the reaction of the ester groups with commercially available α-amino-ω-methoxypoly(oxyethylene) (Jeffamine) according to Scheme 3.

Formation of the amide group proceeded under relatively mild conditions in solution of an excess of Jeffamine at 50 °C without any catalyst. The progress of the reaction could be followed by SEC. After the reaction, an excess of Jeffamine was removed by 3-fold extraction with water. The typical SEC curves of GM−DXP copolymer and the reaction product (graft copolymer) are shown in Figure 2, which indicates that

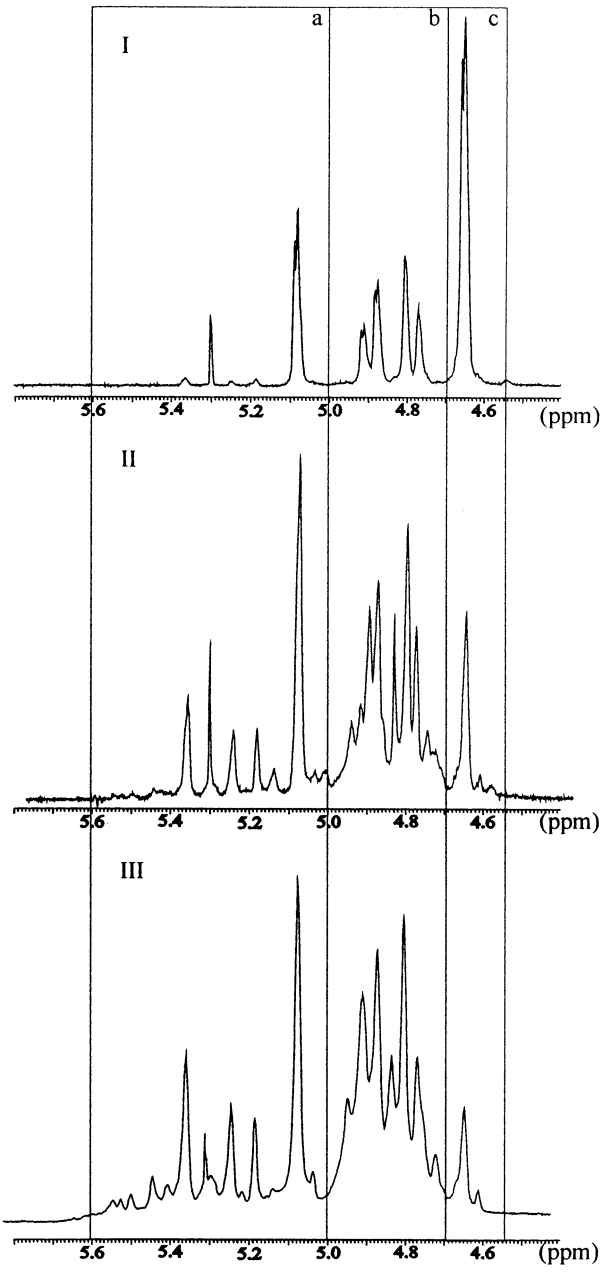


Figure 1. ^{1}H NMR spectra (region of acetal protons absorption only) of GM−DXP copolymers containing different fractions of GM and DXP units. [−GM−]/[−DXP−] in copolymer = 0.27/0.73 (I), 0.44/0.56 (II), and 0.64/0.36 (III): (a) region of absorption of −O−*CH*(COOCH$_3$)−O− groups from GM unit in all regiosequences; (b) region of absorption of −O−*CH*$_2$−O− groups from DXP units in DXP−GM heterodiads; (c) region of absorption of −O−*CH*$_2$−O− groups from DXP units in DXP−DXP homodiads.

molecular weight did indeed increase upon grafting.

For the present work, to characterize graft copolymers as potential modifiers of processes occurring on the surfaces of inorganic crystals, it is essential to know the overall length of the main chain, the number of the ionic groups along the chain, and the number of attached POE side chains. M_n of the precursor chain (GM−DXP copolymer) may be reliably determined by SEC. The composition of precursor copolymer is known from the analysis of ^{1}H NMR spectra. The average number of ester groups per macromolecule can be calculated from known M_n values and known overall compositions.

The degree of conversion of ester groups to amide groups can be determined from ^{1}H NMR spectra. ^{1}H

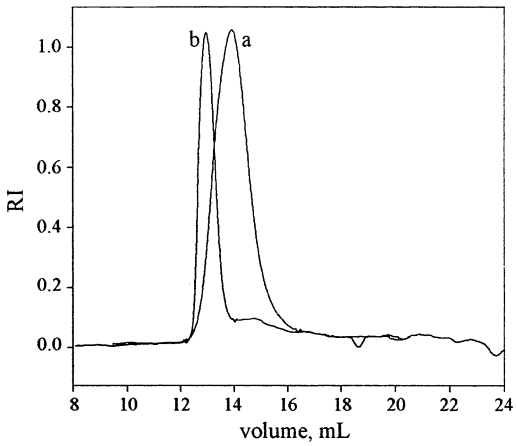
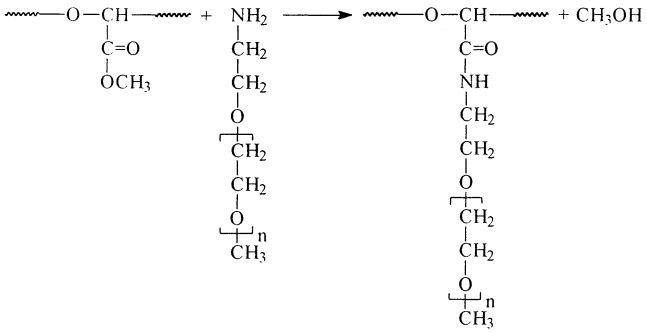


Figure 2. SEC chromatograms of GM−DXP copolymer (purified by reprecipitation with CH_3OH from CH_2Cl_2 solution) (a) and graft copolymer obtained after reaction with Jeffamine (b). Conditions: (a) $[GM]_0 = 3.5$ mol/L, $[DXP]_0 = 1.0$ mol/L, $[TfOH]_0 = 4.3 \times 10^{-3}$ mol/L, CH_2Cl_2, − 30 °C; (b) 1.20 g of GM−DXL copolymer + 3.50 g of Jeffamine ($M_n = 560$), bulk, 50 °C.

Scheme 3



NMR spectrum of the graft copolymer is shown in Figure 3.

Protons of main chain groups and side chains groups are clearly detected, indicating that the product is indeed the graft copolymer. Additional confirmation comes from IR spectra of precursor and the product. In the region characteristic for IR absorption of carbonyl group in the spectrum of the precursor, only one signal with a maximum at 1757 cm^{-1}, corresponding to the C=O bond in the ester group, is present. In the spectrum of the product (at about 50% conversion of ester groups according to ^{1}H NMR) the intensity of the signal at 1757 cm^{-1} is much lower and a new signal appears at 1682 cm^{-1} corresponding to amide groups.

In the next step, the remaining ester groups in graft copolymers were hydrolyzed to carboxylate groups. ^{1}H NMR spectra confirmed complete hydrolysis under the employed conditions (5 wt% solution of KOH in water/acetonitrile; cf. Experimental Section). The fraction of POE side chains did not change, indicating that the amide bond was not cleaved under these conditions. Therefore, the knowledge of M_n, composition (Table 3) and microstructure of precursor DXP−GM copolymers and of the degree of conversion of an ester groups into an amide groups is sufficient to describe the structure of graft copolymer.

Interaction of Graft Copolymers with the Surface of Inorganic Crystals. A direct measure of the interaction of charged molecules with the surface of a crystal is the change of the elektrokinetic (ζ-potential.

Table 3. Average Composition of Graft Copolymers

M_n of the precursor:GM−DXP copolymer (main chain of graft copolymer)	mole fraction of [−GM−] units in the precursor:GM−DXP copolymer	av no. of COO^- groups in a macromolecule of a graft copolymer	av no. of POE chains in a macromolecule of a graft copolymer
4400	0.46	20	1
4400	0.46	18	3
4400	0.46	15	6
3700	0.59	16	6
3700	0.59	14	8
3700	0.59	11	11
8900	0.29	20	8

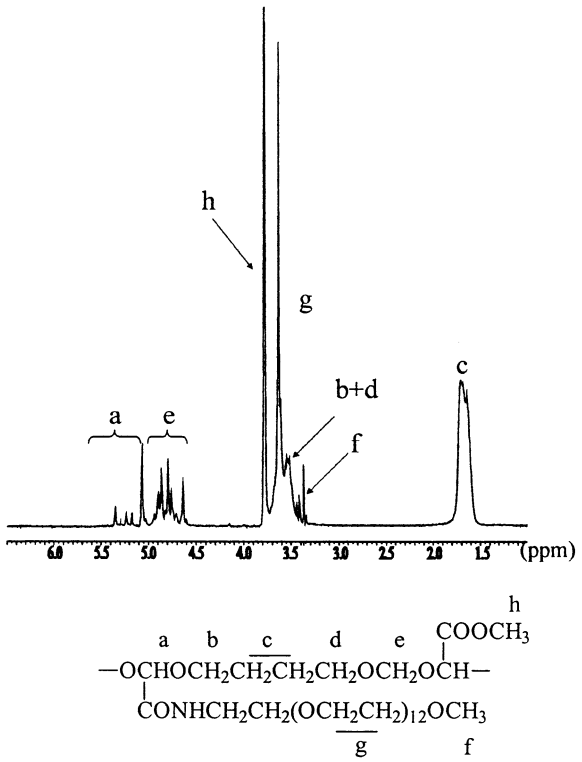


Figure 3. ^{1}H NMR spectrum of graft copolymer. Conditions: GM−DXP copolymer: $[GM]_0 = [DXP]_0 = 2.0$ mol/L, $[TfOH]_0 = 5.8 \times 10^{-3}$ mol/L, CH_2Cl_2, − 30 °C. Graft copolymer: 1.50 g of GM−DXP copolymer + 0.70 g of Jeffamine (M_n = 560). Degree of conversion of ester groups = 9.3%. Assignments are given below the spectrum.

The ζ-potential is a function of the surface charge which develops when a material is placed in a liquid. Although ζ-potential is not a direct measure of surface charge density any adsorbed substances which change the surface will cause changes in the ζ-potential.

The value of the ζ-potential measured for the aqueous suspension of $CaCO_3$ crystals is equal to +29.1 mV. In the presence of solution of graft copolymer, the properties of the surface change considerably, and the surface becomes negatively charged. (ζ = − 33.6 mV.) This result provides a direct proof that negatively charged graft copolymers are indeed adsorbed on the crystal surfaces.

More detailed study on the efficiency of synthesized graft copolymer as modifiers of the processes occurring at the surfaces of inorganic crystals will be published elsewhere.

Conclusions

We have previously shown that stable functional polyacetals may be synthesized by copolymerization of GM with a five-membered cyclic acetal: 1,3-dioxolane (DXL). Significant amounts of mixed cyclic dimer, however, are formed in addition to linear copolymer. In this paper it is shown that copolymerization of GM with a seven-membered 1,3-dioxepane (DXP) proceeds with practically complete conversions of both comonomers and leads to exclusively linear product. Because of the fast transacetalization, comonomer units in copolyacetals are distributed randomly along the chain irrespective of the kinetics of homo- and cross-propagation reactions.

Cationic copolymerization of GM with DXP, proceeding to complete conversion and leading to copolymers with randomly distributed comonomer units, offers thus a convenient method of synthesis of polyacetals in which the number of randomly distributed functional (ester) side groups is simply governed by the composition of the comonomer feed.

Partial substitution of the ester groups with poly(oxyethylene) containing a terminal primary amino group (Jeffamine) led to graft copolymers. The remaining ester group was hydrolyzed giving water-soluble graft copolymers composed of a polyacetal main chain fitted with carboxylate groups and poly(oxyethylene) side chains.

The described sequence of reactions give access to a range of products having the features that are required for polymeric modifiers of processes occurring at the surfaces of inorganic crystals: they are soluble in water and contain ionic groups along the main chain and hydrophilic POE side chains. The degradability of the polyacetal main chain under acidic conditions, which may be desirable for some applications, is an additional advantage of our copolymers.

Acknowledgment. Authors are grateful to Prof. Stanisław Penczek for the valuable comments concerning the interpretation of the results.

Supporting Information Available: Text giving the discussion of the equilibrium concentrations of 7- and 9-membered cyclic dimers, composition of GM−DXP copolymer, analysis of ^{1}H NMR spectra of GM−DXP copolymers, and results of analysis of graft copolymers by triple detection SEC, a table comparing the copolymer and feed compositions, a figure giving the results of the SEC analysis, and schemes showing polymer structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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