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New Poly(Sodium Carboxylate)s Based on Saccharides. II. Cobuilder Performance of Ionic Allyl Glycoside Polymers as Substitutes of Standard Polycarboxylates

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ABSTRACT

New poly(sodium carboxylate)s consisting of neutral or ionic allyl glycoside (AGlu) monomers and maleic acid or itaconic acid as comonomers were examined as substitutes for water-soluble homo- and copolymers of acrylic acid, which are used as cobuilders in detergent formulations. Standardized tests allowed us to measure the calcium sequestering capacity, kaolin dispersing capacity, biodegradability, and thermal stability. These parameters were correlated with the different degrees of functionalization and charge densities of the new polycarboxylates. Comparison with some commercial monomolecular and oligomeric polycarboxylates indicate that the new copolymer poly(allyl- β -D-glucofuranosiduronic acid-co-maleic acid) (P(AGlu-MA)) has an interesting cobuilder performance and is a potentially attractive substitute.

Key Words: Polysaccharides; Polyelectrolytes; Polycarboxylates; Cobuilder; Builder; Calcium sequestering capacity; Kaolin dispersing capacity; Biodegradable polymers.

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INTRODUCTION

Polycarboxylates, such as homo- and copolymers of acrylic acid, are widely used as dispersing agents in many technical applications.^[1,2] They are predominantly used as cobuilders in modern detergent formulations, where cobuilders are defined as low-molecular, water-soluble polymers with high calcium complexation and dispersing properties to prevent incrustation of fibers.^[2-4] Typical examples are acrylic acid polymers with a molecular weight range of 1000–100,000 g/mol. Although these polycarboxylates show an excellent cobuilder performance they are extremely resistant to biodegradation,^[1,2] which is an important aspect for an environmentally acceptable substance. To date there are only a few polycarboxylates that have both biodegradability and the necessary functionality for a cobuilder,^[5,9] e.g., the recently reported poly(aspartic acid) (P(ASP)).^[6-9] This petrochemical based and technical available polymer shows a good biodegradability because of the amide structure, but it does not reach the cobuilder performance of the acrylic acid polymers. Additional critical aspects are the limited thermal and pH stability as well as the supplementary nitrogen transfer into the environment. Also, on a long-term basis no petrochemical raw materials but renewable ones might be used. Therefore, we have developed new polycarboxylates based on carbohydrates that show a favorable ecological profile and preserve natural resources. In a recently published paper, we studied the synthesis and properties of the new polycarboxylates intensively.^[10]

In the present work, the new polycarboxylates of neutral and ionic allyl glycoside (AGlu) monomers and diacids such as maleic acid or itaconic acid were examined with regard to their cobuilder performance, i.e., as essential parameters the calcium sequestering capacity (CaSC) as standard for complexation and the kaolin dispersing capacity (KDC) were determined but also the biodegradability (Zahn–Wellens test) and thermal stability. The cobuilder performance of the new polymers was examined by comparative studies with commercial homo- and copolymers of acrylic acid as well as the biodegradable P(ASP). The classical monomolecular complexing agents EDTA and NTA as well as the new biodegradable iminodisuccinic acid were also used. For the measurements all polycarboxylates were used in the neutralized sodium form and the water content was determined by the Karl Fischer method. The cobuilder properties of the oligomeric polycarboxylates were always examined with polymers of similar molecular weight ($M_w = 5000\text{--}6000\text{ g/mol}$) since an influence of the molecular weight on the parameters could not be excluded. Consequently, a direct comparison between the new and commercial polycarboxylates was possible, whose chemical structures are listed in Table 1.

EXPERIMENTAL

Material and Methods

The following new polycarboxylates based on carbohydrates were synthesized as previously described^[10] (molecular weights, compositions, and water contents are shown in Table 2): poly(allyl- β -D-glucofuranosiduronic acid-co-maleic acid) (P(AGlu-MA)) sodium salt, poly(allyl- α -D-galactopyranoside-co-maleic acid) (P(AGal-MA)) sodium salt and poly(allyl- β -D-glucofuranosiduronic acid-co-itaconic acid) (P(AGlu-IA)) sodium salt.



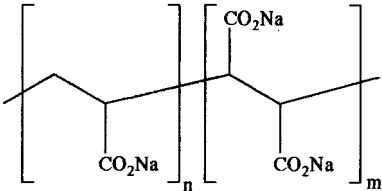
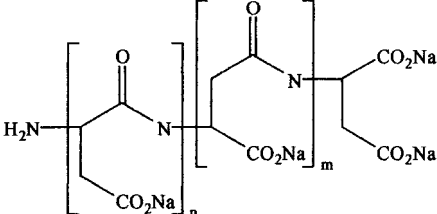
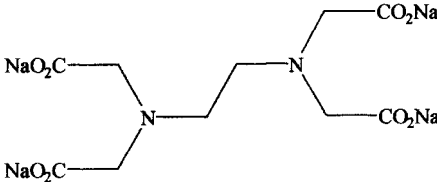
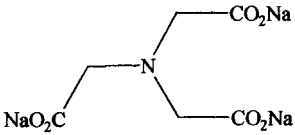
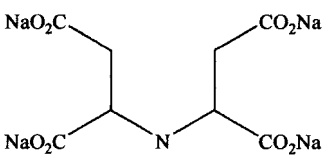
Table 1. Structures of synthesized and commercial poly(sodium carboxylate)s.

Short form	Chemical name	Structure
P(AGlu-MA)	Poly(allyl- β -D-glucofuranosiduronic acid-co-maleic acid) sodium salt	
P(AGal-MA)	Poly(allyl- α -D-galactopyranoside-co-maleic acid) sodium salt	
P(AGlu-IA)	Poly(allyl- β -D-glucofuranosiduronic acid-co-itaconic acid) sodium salt	
P(AA)	Poly(acrylic acid) sodium salt Fluka	

(continued)



Table 1. Continued.

Short form	Chemical name	Structure
P(AA-MA)	Poly(acrylic acid-co-maleic acid) sodium salt Aldrich	
P(ASP)	Poly(aspartic acid) sodium salt Bayer AG	
EDTA	Ethylendiamine-tetraacetic acid tetrasodium salt Fluka	
NTA	Nitrilotriacetic acid trisodium salt Fluka	
IDA	Iminodisuccinic acid tetrasodium salt Bayer AG	

Further polycarboxylates were obtained commercially or were gifts from Bayer AG (molecular weights and water contents are shown in parentheses): poly(acrylic acid) (P(AA)) sodium salt [$M_w = 5700$ g/mol, 7.32 wt% H_2O , Fluka], poly(acrylic acid-co-maleic acid) (P(AA-MA)) sodium salt [$M_w = 4500$ g/mol, 9.35 wt% H_2O , Aldrich], poly(aspartic acid) (P(ASP)) sodium salt [$M_w = 5200$ g/mol, 6.06 wt% H_2O , Bayer AG], iminodisuccinic acid (IDA) tetrasodium salt [9.02 wt% H_2O , Bayer AG], EDTA- Na_4 dihydrate [8.15 wt% H_2O , Fluka], NTA- Na_3 monohydrate [6.88 wt% H_2O , Fluka]. All polycarboxylates were used in the neutralized salt form. The technical samples from Bayer AG were purified by dialysis over two days against deionized water (dialysis tube: MWCO 500 D; Spectra/Por



Table 2. Analytical data of synthesized and commercial poly(sodium carboxylate)s.

Polymer P(M_1 - M_2)	M_w^a (g/mol)	CaSC ^b (mg Ca/g)	Ca-CO ₂ Na	Composition ^c M_1/M_2 (mol%)	w(H ₂ O) ^d (wt%)
P(AGlu-MA)-4	41,300	225.0	0.778	50/50	16.49
P(AGlu-MA)-3	23,400	226.0	0.782	49/51	9.58
P(AGlu-MA)-2	8,900	226.4	0.783	46/54	9.96
P(AGlu-MA)-1	6,400	222.4	0.769	47/53	7.36
P(AGlu-IA)-3	5,900	149.7	0.535	48/52	11.60
P(AGlu-IA)-2	3,700	157.0	0.561	48/52	10.85
P(AGlu-IA)-1	2,400	154.1	0.551	50/50	11.86
P(AGal-MA)-3	10,700	98.5	0.467	49/51	6.64
P(AGal-MA)-2	8,600	102.8	0.487	47/53	8.91
P(AGal-MA)-1	5,800	101.5	0.481	48/52	8.52
P(AA); Fluka	5,700	173.8	0.408	—	7.32
P(AA-MA); Aldrich	4,500	159.6	0.349	70/30	9.35
P(ASP); Bayer AG	5,200	73.4	0.251	—	6.06
IDA; Bayer AG	337	110.5	0.232	—	9.02
EDTA; Fluka	380	129.9	0.308	—	8.15
NTA; Fluka	257	171.2	0.366	—	6.88

^aMolecular weights by GPC-MALLS in buffered 0.3 M NaNO₃ solution at 25°C; P(AGlu-MA): $dn/dc = 0.157$ mL/g; P(AGlu-IA): $dn/dc = 0.146$ mL/g; P(AGal-MA): $dn/dc = 0.162$ mL/g; P(AA): $dn/dc = 0.190$ mL/g; P(AA-MA): $dn/dc = 0.180$ mL/g; P(ASP): $dn/dc = 0.163$ mL/g.

^bCalcium sequestering capacity (CaSC). Conditions: pH 10; 25°C.

^cCopolymer composition from ¹³C-NMR.^[10]

^dRemaining moisture determined by Karl Fischer method.

CE-Membrane; SPECTRUM). All other reagents were analytical-grade commercial products and used without further purification.

General Measurements

¹³C-NMR spectra for the polymers were recorded on a BRUKER WM 400 spectrometer using the inverse gated decoupling technique with the following conditions: 100.6 MHz; acquisition time 0.492 s; delay 5 s; 12,000 scans; 90° impulse; solvent D₂O (0.1 g monomer/0.7 mL D₂O); 25°C. The water content of the polymers was measured by the Karl Fischer method using a titration apparatus (METROHM). Samples were transferred to a titration vessel containing a mixture of 80 mL formamide (MERCK) and 20 mL Karl Fischer solvent (MERCK; No. 9241). The titration with Karl Fischer titrant (MERCK; No. 9243) was carried out automatically using the dead-stop technique.

Molecular Weight by GPC-MALLS

Average molecular weights (M_w and M_n) and molecular weight distribution (M_w/M_n) were measured on a GPC-MALLS apparatus (Waytt Technology) incorporating a set of



separation columns (TSK G 5000 PW_{XL} + TSK G 4000 PW_{XL} + TSK G 3000 PW_{XL}) coupled with a multi-laser light scattering detector (MALLS). The light source was a He–Ne laser of 632.8 nm. The measurements were recorded at 25°C with a flow rate of 1 ± 0.1 mL/min using a buffered eluent consisting of 0.08 M *tris*(hydroxymethyl)aminomethane (TRIS) + 0.30 M NaNO₃ + 0.01 M NaN₃ adjusted to pH 7 with nitric acid. All polymer samples were used as stoichiometrically neutralized sodium salts and injected as 1 wt% solutions filtered through a Whatman filter (0.02 μm).

Specific Refractive Indices

The specific refractive index increments were measured at 25°C on a BRICE-PHOENIX BP-2000 V differential refractometer (VIRTIS) with a laser of wavelength 632.8 nm. The required dialysis of the polymer solution against a large volume of solvent was performed with dialysis bags of 500 D MWCO (Spectra/Por DispoDialyzer; SPECTRUM) to avoid polymer loss. The solvent was the above buffered NaNO₃ solution.

Calcium Sequestering Capacity

A solution of 0.1 g neutralized polycarboxylate in 60 mL deionized water was adjusted to pH 10 with 0.1 M sodium hydroxide solution. A 5 mL of 0.1 M potassium oxalate solution was added and the polymer solution was pumped at 25°C through a photometer cell (type LTP 5, Dr. LANGE). The 0.1 M calcium chloride solution was added continuously with a Dosimat (type 665, Metrohm) until a permanent turbidity remained. During titration the pH value was monitored and held constant automatically with a Dulcometer PHD (PROMINENT) connected with a pH electrode. Consumption of calcium chloride solution was determined graphically from the titration curves according to the tangent method. The 1 mL of the added 0.1 M calcium chloride solution corresponds to a sequestering capacity of 40.08 mg Ca(II)/g poly(sodium carboxylate). All CaSC values were corrected to take into account the remaining moisture of the hygroscopic polycarboxylate samples.

Kaolin Dispersing Capacity

The kaolin type HI SPEZIAL (DORFNER, Germany) was used as a model substance for inorganic solid particles (HI SPEZIAL characteristic: specific surface: 9.5 m²/g; Ø = 1.3 μm). For the experiments 1 wt% kaolin dispersions were prepared by intermixing 10 g of kaolin in 1 L deionized water at 25°C for 10 min by means of a magnetic stirrer (400 rpm) and adjusting the pH to 7. Then, from the stock solutions of the different polycarboxylates (1 mg polymer/mL; considering remaining moisture) the corresponding volumes were added to the kaolin batches, so that polymer concentrations of 20–150 ppm (mass polymer per mass kaolin) resulted. It was stirred for a further 10 min during which the pH value was controlled and if necessary again adjusted to pH 7. The dispersions were then filled into Imhoff funnels and after 1 h the sediment volume was read off. For a blank value a batch without polymer was measured under the same conditions. The volume



difference of the sediments of the batches with and without polymer after 1 h corresponds to the KDC as a percentage.

Aerobic Biodegradation Test

The biodegradability of the polycarboxylates was determined by the modified Zahn–Wellens test.^[14] Each test series was run in parallel with the test substance, the reference substance sodium acetate for testing the inoculum activity and a blank control (containing only activated sludge). The weighed portions of the test substance and of the reference substance were selected in such a way that an initial chemical oxygen demand (COD) of ~ 700 mg/L occurred. The substances were dissolved in 1 L deionized water, adjusted to pH 7 and added with mineral nutrients. The blank control was treated in the same way. Activated sludge, freshly obtained from the municipal sewage plant in Braunschweig-Watenbüttel (Germany), was added to the incubation vessels (DS: 0.3 g/L) and the mixtures were agitated and aerated at 25°C in the dark for up to 42 days. The biodegradation process was monitored by determining the COD of filtered samples taken at weekly intervals. The degree of biodegradation as a percentage was expressed as the eliminated COD, corrected for the blank, to the initial difference of the COD values of substance and blank after 3 h.

RESULTS AND DISCUSSION

Calcium Sequestering Capacity

As a main parameter for cobuilder properties, the CaSC were measured. These weight to weight quantities show the efficacy of sequestering agents and are particularly important from a practical point of view for detergent formulations.^[2–4] The CaSC values were

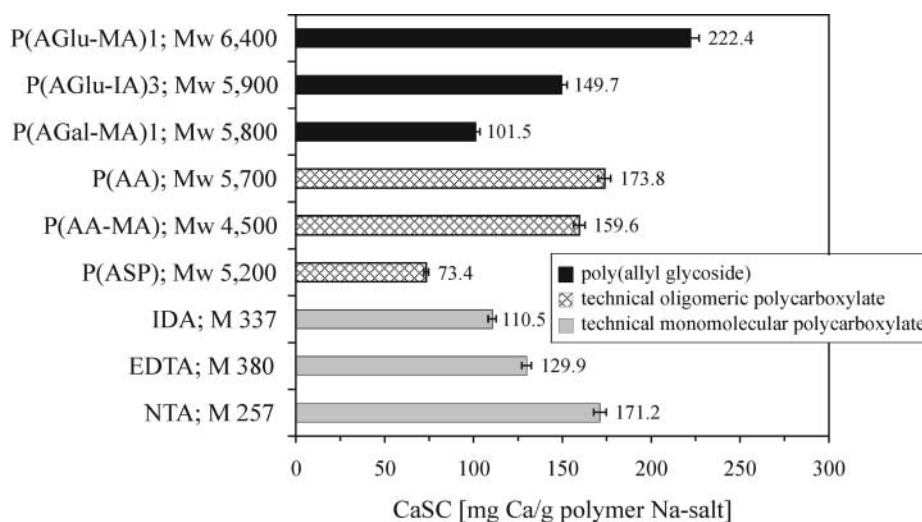


Figure 1. Calcium sequestering capacities of different polycarboxylates at pH 10 and 25°C.



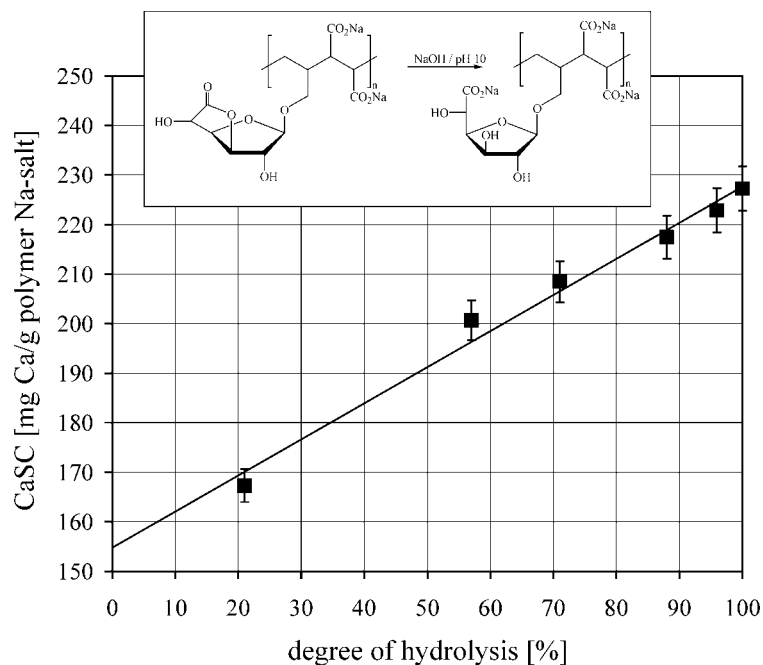


Figure 2. Calcium sequestering capacities as a function of the degree of hydrolysis of the lactone rings in P(AGlu-MA). Conditions: 25°C; pH 10.

determined by turbidimetry using potassium oxalate as indicator salt according to Wilham and Mehlretter.^[11] The endpoint of titration of the polycarboxylates with calcium chloride solution was achieved when a permanent turbidity remained. The CaSC values are defined as mg Ca(II) sequestered per gram poly(sodium carboxylate). In addition to the maximum CaSC values the influence of degree of functionalization, charge density, and molecular weight on CaSC were also examined. These studies were possible based on structurally different allyl glycoside copolymers. The results are presented in Figs. 1–4 and summarized in Table 2.

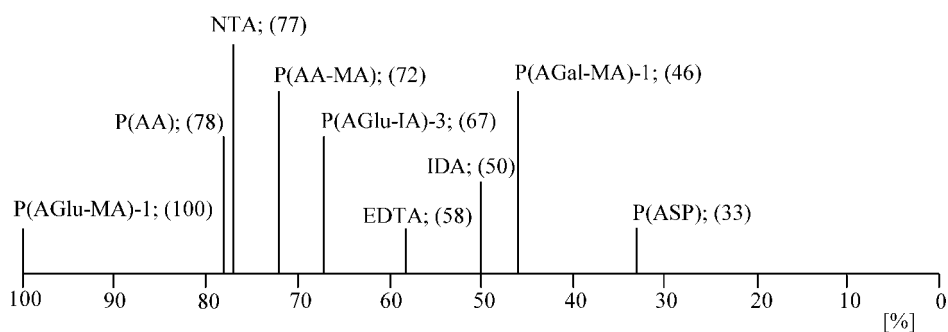


Figure 3. Calcium sequestering capacities of different polycarboxylates on a relative scale (percentage in parentheses).



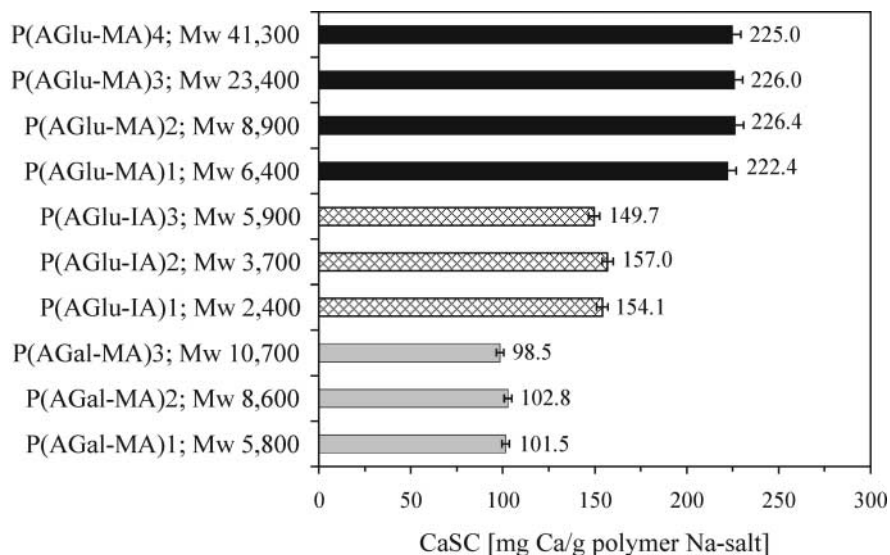


Figure 4. Calcium sequestering capacities of allyl glycoside copolymers as a function of the molecular weight. Conditions: 25°C; pH 10.

The alternating ionic AGlu copolymers^[10] show significant differences in their CaSC values and are dependent on the chemical structure of the comonomers. The copolymer P(AGal-MA), with two carboxyl groups per repeat unit, shows a CaSC value of 102 mg Ca/g. On the other hand, the copolymer P(AGlu-MA) has a CaSC value of 222 mg Ca/g. Consequently, the introduction of a further carboxyl group per repeat unit by substitution of the neutral allyl galactopyranoside (AGal) with an ionic AGlu leads to a doubling of the CaSC value. This significant improvement of the CaSC should be highlighted as the commercial P(AA), P(AA-MA), and P(ASP) show considerably smaller CaSC values (174, 160, and 73 mg Ca/g, respectively). Also, the classical monomolecular polycarboxylates EDTA and NTA as well as the new IDA show far smaller values (130, 171, and 111 mg Ca/g, respectively). In Fig. 3, these CaSC values are shown on a relative scale.

The stoichiometric composition of the complex structure was calculated from the CaSC values and is expressed as the number of calcium ions per carboxyl group (see Table 2). The required unambiguous polymer constitution has been determined previously.^[10] Essentially, intermolecular Coulomb interactions have to be assumed between calcium cation and several anionic coordination locations along the polymer chain. From the experimental CaSC value of P(AGlu-MA) two calcium ions are complexed per repeat unit, i.e., with three carboxyl groups. The maleic acid and the ionic allyl glycoside are complexing one calcium ion as chelate in each case. This ratio of two Ca(II) ions per three carboxyl groups corresponds to the maximum sequestering capacity that is achieved only upon complete ring opening of the lactone rings in the polymer chain (see Fig. 2; analysis by NMR^[10]). The analogous calculation for the copolymer P(AGal-MA) shows that one calcium ion is complexed per maleic acid unit, i.e., with two carboxyl groups. Consequently, the maximum sequestering capacity is achieved for both copolymers for which the favorable distribution of the carboxyl groups along the polymer



chain might be responsible. For the high charge density polymer P(AA) the maximum sequestering capacity is not achieved and only 0.8 calcium ions are bound to the two closely arranged carboxyl groups. This limiting effect is also observed for copolymer P(AA-MA) that has an even higher degree of functionalization but no better CaSC value. Similar effects were also reported by Ragnetti.^[12] Accordingly, the excellent CaSC of copolymer P(AGlu-MA) arises from both the high degree of functionalization and the reduced charge density, i.e., the moderate distance between the carboxyl groups caused by the carbohydrate moieties. These results might be helpful for the design of advanced cobuilders in the future.

It is interesting to note that the CaSC values of the allylic copolymers examined are independent of the molecular weight in the investigated range ($M_w = 2400\text{--}41,300$ g/mol; see Fig. 4). Below weight-average molecular weights of 1000 g/mol a reduction of the properties is observed. A comparable effect was already mentioned for oxidized polysaccharides in prior literature.^[13] Therefore, the investigated pure allylic carbohydrate monomers are not usable as cobuilders.

Kaolin Dispersing Capacity

Low-molecular polycarboxylates stabilize colloidal dispersions preventing precipitation in detergent formulations. Hence, the dispersing capacity is a further basic parameter and has been determined by sedimentation experiments. Here, the dispersing capacity is defined as the percentage of solid matter that can be held in suspension by addition of a polymer under defined conditions for over 1 h. The clay mineral kaolin was used for preparing model dispersions as it has a defined particle size, chemical stability, and a good dispersibility in water. For comparative studies, defined dispersions were prepared with 1 wt% kaolin at 25°C, pH 7 and stirring at constant shearing. A constant pH is important as this influences the degree of dissociation of the carboxyl groups and the surface charge of the kaolin particles. The polymer concentration was varied within the range 20–150 ppm. The KDCs of the different oligomeric polycarboxylates as function of the polymer concentration are presented in Fig. 5.

Obviously, the favored copolymer P(AGlu-MA) shows a good dispersing capacity comparable with the commercial polymers of the acrylic acid. These polymers already have the maximum dispersing capacity of 90% at a polymer concentration of 50 ppm. An increase of the polymer concentration to 150 ppm led to no improvement as the kaolin used contained a coarse-grained fraction that could not be stabilized. On the other hand, the allyl glycoside copolymers P(AGal-MA) and P(AGlu-IA) as well as the aspartic acid polymer P(ASP) show a 20–30% smaller dispersing capacity. Only by doubling the polymer concentration to 100 ppm the same stabilization effect achieved. The different stabilization of the dispersions results from a modified electric double layer, whose layer thickness and structure is influenced by the different degrees of functionalization and charge densities of the adsorbed polycarboxylates. This is especially obvious in comparing the poly(allyl glycoside)s P(AGal-MA) and P(AGlu-MA) with two and three carboxyl groups, respectively per repeat unit. The removal of one carboxyl group per unit leads to a reduction of the dispersion capacity by 20%, which illustrates again the importance of substitution of a neutral by an ionic component in the otherwise structurally analogous allyl copolymers.



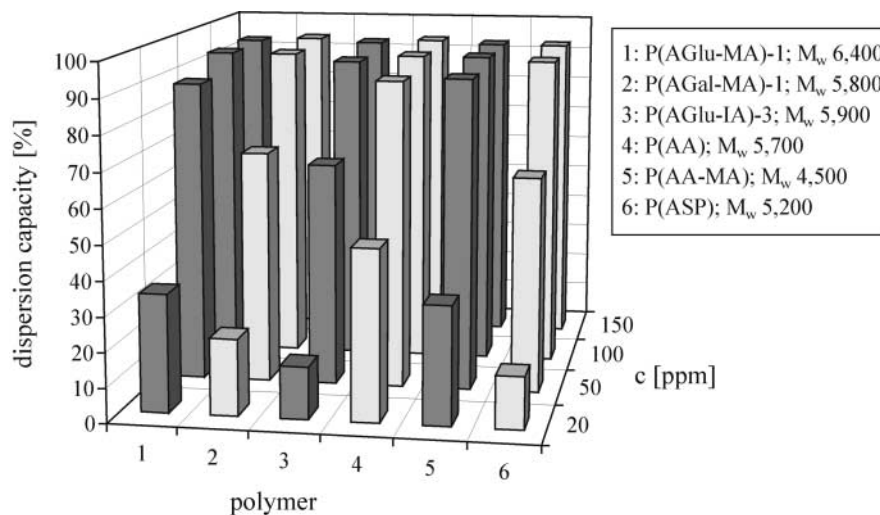


Figure 5. Kaolin dispersing capacity of different polycarboxylates as a function of polymer concentration (referring to kaolin) measured after 1 h sedimentation. Conditions: pH 7; 25°C.

Thermal and pH Stability

Subsequently, a stability study of the most suitable copolymer P(AGlu-MA) with a molecular weight of $M_w = 7300$ g/mol was performed to assess its dependence on temperature and pH in a commercially interesting range. Samples were taken over a period of 10 h in a temperature range of 30–60°C and pH 7–10. These samples were neutralized and freeze-dried without previous dialysis. Degradation reactions could be examined by means of GPC-MALLS as by-products could be quantified chromatographically and changes in molecular weight could be detected. The studies were accompanied by ^{13}C -NMR spectroscopy for controlling the copolymer composition (method: see lit.^[10]). The temperature, pH, and time dependency of the percentage recoveries of the copolymer are depicted in Fig. 6. These indicate that the copolymer is unchanged under neutral and alkaline conditions as there are few by-product portions (<1%) and the molecular weight remains constant. Furthermore, the constant copolymer composition of 1 : 1 established by NMR spectroscopy shows, that no appreciable chemical degradation reactions occur in the monosaccharide side chain of the polymer. Thus, the new polycarboxylate P(AGlu-MA) appears to be stable over the entire range studied.

Biodegradation Test

In addition to the cobuilder application test, the biodegradability of the different polycarboxylates was examined. The modified Zahn–Wellens test,^[14] which works at high inoculum concentration and continuous aeration, was used to determine the inherent biodegradability. The test substances were examined over a period of 42 days under standard conditions by taking samples weekly and monitoring the decrease of COD. The



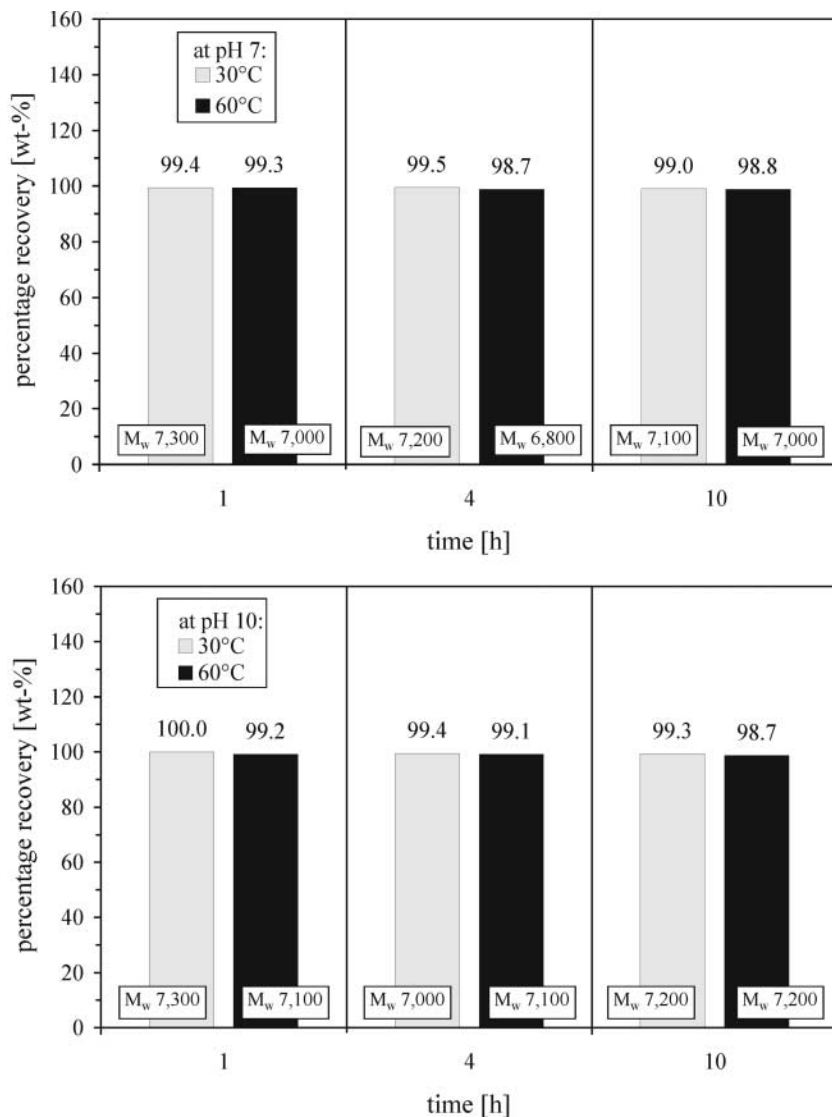


Figure 6. Stability of the copolymer P(AGlu-MA) ($M_w = 7300$ g/mol) as a function of temperature and time. Conditions: pH 7 and 10.

degree of biodegradation (DB) is expressed as a percentage by comparing the eliminated COD, corrected for the blank, to the initial difference of the COD values of substance and blank. The results are presented in Figs. 7 and 8.

The comparison of the DB values of poly(allyl glycoside)s and commercial polycarboxylates shows that P(ASP) and IDA are readily biodegradable (DB = 80–90%). The degradation curves show the typical triadic structure of lag phase, degradation phase, and plateau phase. On the other hand, the P(AA) is not biodegradable which confirms literature trends^[1,2] (DB = 2–4%).



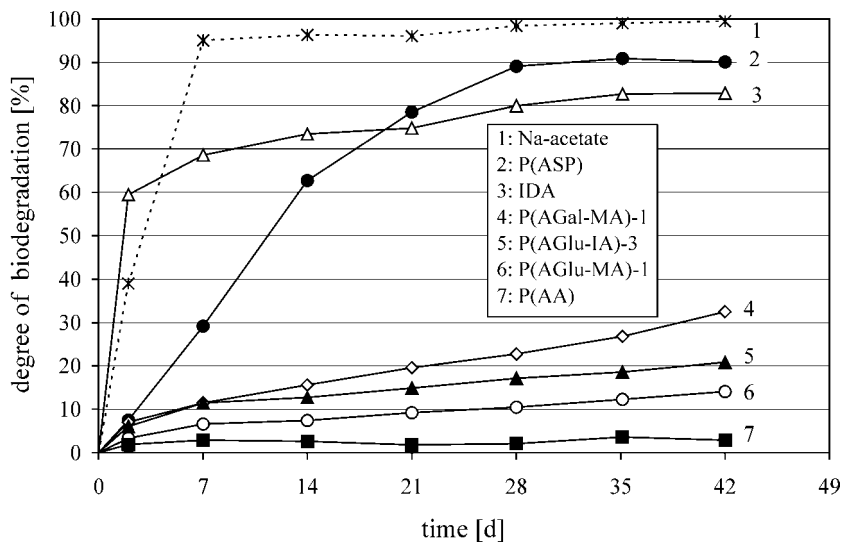


Figure 7. Biodegradation curves of polycarboxylates determined by the modified Zahn–Wellens test. Reference: sodium acetate. Conditions: pH 7; 25°C; activated sludge concentration: 0.3 g DS/l.

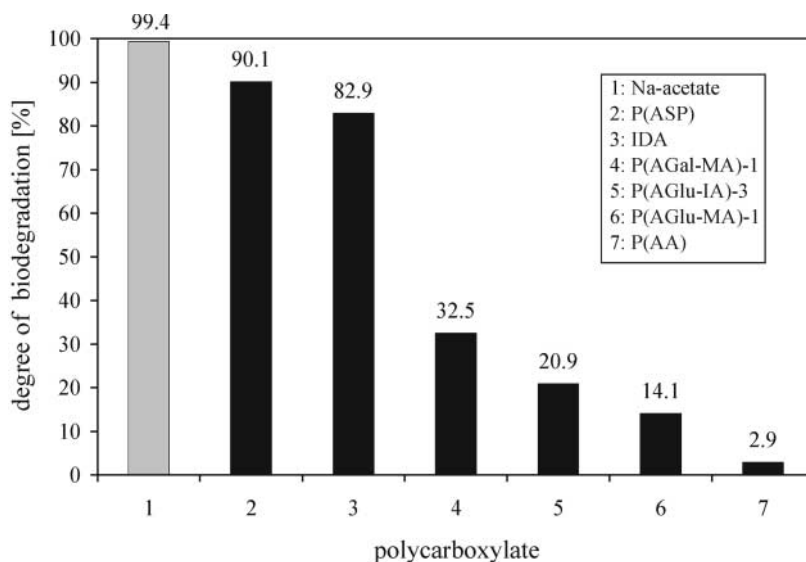


Figure 8. Degrees of biodegradation of polycarboxylates after 42 days determined by the modified Zahn–Wellens test. Reference: sodium acetate. Conditions: pH 7; 25°C; activated sludge concentration: 0.3 g DS/l.

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The new poly(allyl glycoside)s P(AGlu-MA), P(AGlu-IA), and P(AGal-MA) show better degradation values (DB = 14–33%) than P(AA), but do not achieve the level of the P(ASP). Obviously, a clear improvement in degradation behavior results from decreasing the functionalization and the charge density, respectively. This is indicated by the structurally similar copolymers P(AGlu-MA) and P(AGal-MA), which differ only in one carboxyl group in the saccharide side chain. The lower degree of functionalization in the polymer P(AGal-MA) results in a doubling of the DB value. A similar trend was already described for oxidized polysaccharides in the literature.^[15,16] Consequently, the interesting copolymer P(AGlu-MA) shows a limited degradation and cannot be described as inherently biodegradable. Clearly for the polycarboxylates examined a compromise has to be found between a good cobuilder performance, determined by functionalization, and the decreasing degree of DB.

CONCLUSION

The new water soluble polycarboxylate of the ionic allyl monomer AGlu and maleic acid presented in this study shows an interesting cobuilder performance and is favored as a potentially attractive substitute of commercial copolymers of acrylic acid. The copolymer shows an excellent CaSC which arises from both the high degree of functionalization and a favorable charge density distribution along the polymer chain. An influence of the molecular weight on the CaSC values is not observed in the investigated range. The dispersing capacity is comparable with that of acrylic acid copolymers and for a commercially interesting range, a sufficient thermal and pH stability is found. The biodegradation tests show that an increase of the degree of functionalization results in a decrease of the degree of DB so that a compromise has to be found between a good cobuilder performance and the DB behavior.

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