Synthesis and Properties of Hydrophilic Polymers, Part 11: Synthesis, Biodegradability, and Metal Complexation of Copolymers of Ethylenediaminetetraacetic Acid Dianhydride and Lactose

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ABSTRACT: The synthesis and characterization of poly (ethylenediaminetetraacetic acid-*co*-lactose) of high molar mass (132 kg mol^{-1}) is described. The polycondensate with pendant carboxylic groups was shown to be hydrolytically and microbiologically degradable by using conventional microbiological methods. The metal complexing properties of the polyester were studied for Cr(III), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Sr(II), Cd(II), Pb(II), and Al(III) ions in aqueous solution using the liquid-phase polymer-based retention (LPR) method. In addition, the complexing capacity of the Cu(II)-saturated copolymer was determined by TGA to be 182 mg g^{-1} polymer. According to the retention profiles determined as a function of filtration factor by using LPR in conjunction with inductively coupled plasma spectrometry, Cr(III) and Fe(III) showed a strong interaction with this polymer under these conditions, indicated by retention values of 100% at pH 5. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 2932–2939, 2007

Key words: biodegradable; metal–polymer complexes; water-soluble polymers

INTRODUCTION

Incorporation of chelating ligands into polymers via condensation polymerization is well-known as one suitable method for chelating polymers. Prime examples have included polymers formed by the condensation of formaldehyde with reactive phenols and/or amines.[1–4] Other types are common condensation reactions such as polyester and polyamide formation; for example, a series of polyamides formed by the condensation of ethylenediaminetetraacetic acid (EDTA) anhydride with various diamines[5] by using a number of organic ligands containing amino-acetic acid groups (—$NHCH_2COOH$) or iminodiacetic acid groups [—$N(CH_2COOH)_2$] are known to form stable complexes with a variety of metal ions.[6] Recently, carboxy-functional polyesters based on poly(ethylene glycol) and oligofunctional carboxylic acids such as ethylenediaminetetra-acetic acid and diethylenetriaminepenta-acetic acid, which represent promising candidates for the preparation of environmentally degradable polycondensates, have been reported.[7]

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The separation and enrichment of hazardous metal ions in aqueous solutions play an important role for their removal in municipal and industrial wastewater. Among many separation techniques, membrane separation is an efficient and widely applied separation process that is comparable to other separation techniques in terms of technical and economical feasibility.[8,9] On the other hand, many commercial separation problems are being solved by membrane processes, which can be successfully used to treat industrial effluents.

Classical preconcentration and separation methods for elements in geological, biological, environmental, and industrial fluids are liquid–liquid extraction, sorption, precipitation, ion exchange, and others. However, these two-phase processes involve disadvantages such as reactions in heterogeneous phase and long contact times. The efficient and selective separation of inorganic ions can be achieved by water-soluble, polymeric reagents in combination with membrane filtration. This technique developed in our laboratory, called liquid-phase polymer-based retention (LPR), is based on the separation of ions bound to water-soluble polymers with chelating groups (polychelatogens) from noncomplexed ions.[10–12] It has found application in the recovery of metals from diluted solutions both on an analytical and technical scale.

A variety of soluble polymers have been studied for homogeneous-phase applications such as derivatives

of poly(ethylenimine),[13] poly(vinylamine),[14] poly(acrylic acid-*co*-acryl amide),[15] polychelatogens based on polyurethanes, poly(vinyl alcohol), as well as different other copolymers. Previously, we have investigated hydroxy-functional polymers based on aziridine, showing that poly[1-(2-hydroxyethyl) aziridine] containing hydroxyl groups in the side chain are able to bind a number of metal ions.[16] Recent studies of our group include also the synthesis of environmentally degradable chelating polymers based on ethylenediaminetetra-acetic acid (EDTA)[7] and on aspartic acid such as poly[(2-hydroxyethyl)-DL-aspartamide].[17]

In this study, we report the polycondensation, characterization, and microbiological degradation of ethylenediaminetetra-acetic acid dianhydride and lactose and additionally the metal complexing properties of this novel copolymer.

EXPERIMENTAL

Materials

Ethylenediaminetetra-acetic acid dianhydride (EDTA-DA) (Aldrich, 98%) and D-lactose (Sigma, min. 99%) were used after drying at 60°C under vacuum. Formamide (Aldrich, 99+%) was dried before use. All metal salts were used in the form of nitrates and purchased from Junsei, except of Ni(II) (Aldrich), Cr(III) (Janssen), Pb(II) and Sr(II) (Yakuri). K_2HPO_4 (Aldrich, 98+%), KH_2PO_4 (Oriental Chemical Industry (OCI), extra pure), $(NH_4)_2SO_4$ (OCI, extra pure), $MgSO_4 \cdot 7H_2O$ (OCI, extra pure), Dextrose (OCI, anhydrous), Bactoagar (Difco), $ZnSO_4 \cdot 7H_2O$ (Aldrich, reagent), $FeSO_4 \cdot 7H_2O$ (Aldrich, reagent), EDTA disodium salt (Aldrich, reagent), $MnSO_4 \cdot H_2O$ (Sigma, ACS reagent), $CuSO_4$ (Aldrich, 98%), $Co(NO_3)_2 \cdot 6H_2O$ (Aldrich, reagent), and $Na_2B_4O_7 \cdot 10H_2O$ (Aldrich, reagent) were used as received.

The *Pseudomonas* basal mineral medium consisted of K_2HPO_4 (12.5 g), KH_2PO_4 (3.8 g), $(NH_4)_2SO_4$ (1.0 g), $MgSO_4 \cdot 7H_2O$ (0.1 g), anhydrous dextrose as a carbon source (0.8*M*, 100 mL), and 5.0 mL of trace element solution ($ZnSO_4 \cdot 7H_2O$ (1.1 g)), $FeSO_4 \cdot 7H_2O$ (0.5 g), EDTA disodium salt (0.29 g), $MnSO_4 \cdot H_2O$ (0.154 g), $CuSO_4$ (0.026 g), $Co(NO_3)_2 \cdot 6H_2O$ (0.025 g), and $Na_2B_4O_7 \cdot 10H_2O$ (0.018 g) in 100 mL distilled water.

Instruments and methods

FTIR spectra (KBr pellets) were recorded on a Perkin-Elmer 2000 series and ^{1}H-NMR spectra on a JEOL JNM-LA 300 WB FT-NMR spectrometer (300 MHz). Molecular masses were measured by light-scattering measurements (Malvern 4700C). Thermal gravimetric analysis was performed with a TGA 2050 (TA Instruments), and the concentrations of metal ions were determined by inductively coupled plasma spectrometry (ICP, Thermo-Jarrell Ash IRIS/AP). For the microbiological degradation experiments, the turbidity was measured by a turbidimeter (HS Scientific, Portable Turbidirt DRT-15CE), and an autoclave (Auto Clave DAC 811) and a clean bench (DVB 912) of Daeil Engineering were also used. The morphological features were measured by a scanning electron microscope (JEOL, JSM-5800). For the measurement of hydrolytic degradation, a micro Ubbelohde viscometer with suspending ball-level (Schott-Geraete) was used. Carboxyl groups were determined by using a titrator (Metrohm 702 SM Titrino).

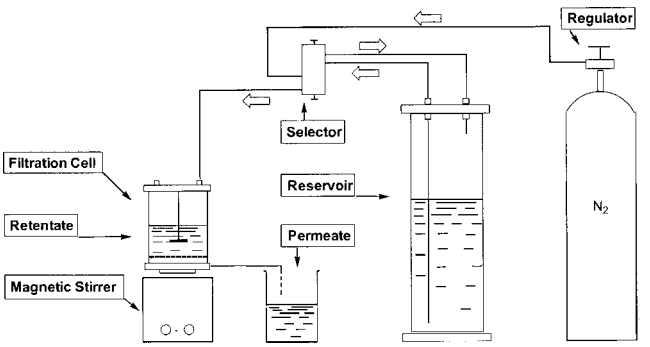


Figure 1 Experimental set-up of the membrane filtration system for the complexation studies in aqueous solution using the liquid-phase polymer-based retention (LPR) technique.

Membrane filtration was carried out with a system as described previously.[18] The membrane filtration unit consisted of a membrane filtration cell, containing the polymer solution, to which the solution of metal ions was added under stirring. For continuous separation, the washing solution was passed from the reservoir to the cell (Fig. 1).

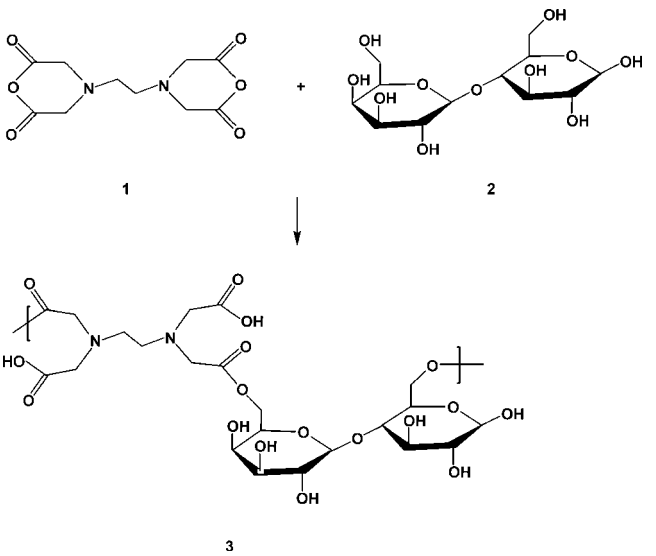
For the kinetic analysis of decomposition of the polymers and polymer–metal complexes the following models were used:

$$\text{Coats} - \text{Redfern}^{19}: \ln\frac{f(\alpha)}{T^2} = \ln\left[\frac{AR}{\beta E}\left(1 - 2\frac{RT}{E}\right)\right] - \frac{E}{RT}$$

$$\text{van Krevelen}^{20}: \ln f(\alpha) = \ln\left[\frac{A}{\beta}\left(\frac{0.368}{T_{\max}}\right)^{\frac{E}{RT_{\max}}}\left(\frac{E}{RT_{\max}} + 1\right)^{-1}\right] + \left(\frac{E}{RT_{\max}} + 1\right)\ln T$$

$$\text{Broido}^{21}: \ln f(\alpha) = \ln\left[\frac{A}{\beta}\frac{R}{E}T_{\max}^2\right] - \frac{R}{E}\frac{1}{T}$$

where the ratio of actual weight loss to total weight loss corresponding to the degradation process (α), $\alpha = (w_0 - w)/(w_0 - w_f)$, w_0 is the initial weight, w the weight at



Scheme 1 Polyreaction of ethylenediaminetetra-acetic acid dianhydride (EDTA-DA) (1) and D-lactose (2) yielding poly(ethylenediaminetetraacetic acid-*co*-lactose) (PEL) (3).

temperature T, w_f the final weight, $f(\alpha)$ a function of α, β the heating rate (deg min^{-1}), T_{max} the temperature of maximum rate of weight loss (K), E the activation energy (kJ), and A is the frequency factor (s^{-1}). The entropy was calculated from the equation of $A = (kT_{max}h^{-1})$ $(e^{\Delta S/R})$, where k is the Boltzmann's constant, h is the Planck's constant, and R is the gas constant.

Synthesis of poly(ethylenediaminetetra-acetic acid-*co*-lactose)

D-Lactose (1.130 g, 3.3 mmol) was dissolved in 10 mL of freshly dried formamide, and a suspension of ethylenediaminetetra-acetic acid dianhydride (EDTA-DA, 0.846 g, 3.3 mmol) in 10 mL of freshly dried formamide was prepared (Scheme 1). To this suspension, the lactose solution was added dropwise and the mixture was heated to 60°C under reflux and UV monitoring. During the polyreaction, the suspension changed to a clear, transparent, and slightly yellow liquid after 27 h. When reaching the maximum absorbance during the UV monitoring, the mixture was cooled and precipitated into ethanol using a 10-fold excess. After the precipitation, the polymer was filtered and dried using rotary evaporator. The product was then dissolved in 70 mL water, neutralized with 0.1*M* sodium hydroxide, freeze-dried to a white solid after purification by membrane filtration (Amicon YM1 membrane, nominal molar mass exclusion limit of 1 kg mol^{-1}). Yield: 0.654 g (33%, retention of $M > 1$ kg mol^{-1}).

Titration

For the determination of carboxyl groups in the polymer, a polymer solution (50 mL, 2.5 mg) was prepared. The content of free carboxylic acid in the polymerization was determined by titration using 0.05*N* NaOH.

Microbiological degradation of poly(ethylenediaminetetra-acetic acid-*co*-lactose)

Enrichment and isolation

A mixed culture was collected from the soil of the K-GIST campus at ground surface and pond bed and from the activated sludge of the Kwangju municipal sewage treatment plant. The mixed culture was filtered with 6 μm filter paper and added to the polymer solution containing 100 mg poly(ethylenediaminetetra-acetic acid-*co*-lactose) (PEL) in 150 mL solution (ratio of mineral medium to phosphate buffer was 1 : 2). For microbiological enrichment, the mixed culture was acclimated to the polymer solution at constant temperature (25°C) under stirring.

Batch test for polymer degradation

A solid medium for colony-forming unit enumeration as a the first step was prepared with the solution of 100 mg polymer and 40 mg agar (4 wt %) in 1 L phosphate buffer (pH 7.2), sterilized in an autoclave at 121°C for 15 min, cooled to 40°C, poured into sterilized petri dishes, dried in a clean bench by UV irradiation, and stored at 4°C before use. For the inoculation, 1 mL of the enriched mixture culture acclimated to the polymer was added to the PEL solution (0.008 wt % of phosphate buffer), and then the inoculated solution was stirred at 25°C. To monitor the degradation process based on microbial growth, 100 μL aliquots were collected from the inoculated solution, diluted 10-fold to test tubes, and spread on the solid medium.

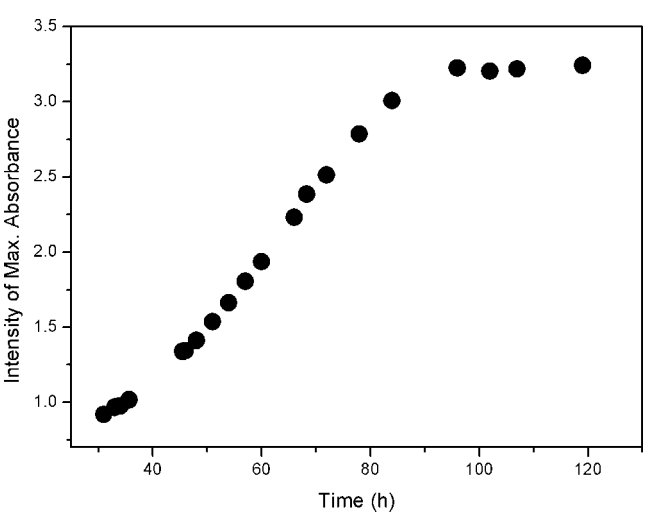


Figure 2 UV-monitoring of the reaction time for the polyreaction of EDTA-DA and D-lactose.

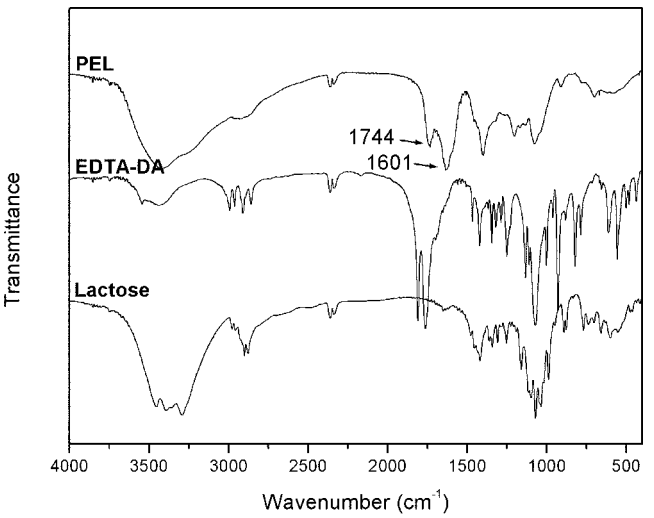


Figure 3 FTIR spectra of (a) poly(ethylenediaminetetraacetic acid-*co*-lactose) (PEL), (b) ethylenediaminetetra-acetic acid dianhydride (EDTA-DA), and (c) D-lactose.

Then, the colony-forming units were counted and assessed as an indicator for degradability.

Metal complexation studies

For the determination of the complex binding ability, a solution of the 10 metal nitrates was placed into the filtration cell containing the polymer solution. The volume in the cell was kept constant at 20 mL with a concentration of the polymer of 1 wt% and a metal ion of each concentration 20 mg L^{-1}. The pH of the cell and the reservoir solutions were adjusted to pH 5, and the system was pressurized with N_2. A membrane with a nominal molar mass cut-off (MMCO) of 1 kg mol^{-1} (Amicon YM1) was used. The filtrate fractions ($Z = 1$–10) were collected and subjected to analysis by inductively coupled plasma spectrometry.

For the thermal stability studies of a metal-saturated sample by TGA, a Cu(II) nitrate solution (2 wt %, 10 mL) was added to the polymer solution (1%, 10 mL) under stirring. The mixture obtained was membrane filtrated, and then the retentate was freeze-dried.

RESULTS AND DISCUSSION

Synthesis

PEL was prepared in an one-step polyreaction of ethylenediaminetetra-acetic acid dianhydride (EDTA-DA) and lactose in formamide. The molecular mass was found to be 132 kg mol^{-1} by light scattering measurement after removing low-molecular constituents from the higher molecular mass fractions (>1 kg mol^{-1}) by membrane filtration. The incorporation of iminodiacetic acid derivatives such as ethylenediaminetetra-acetic acid (EDTA) and diethylene triamine penta-acetic acid (DPTA) can produce chelate-forming polymers able to bind many multivalent metals.[22] Water-soluble carboxy-functional polyesters based on poly(ethylene glycol) with EDTA or DPTA incorporated into the polymer backbone were described.[7] In contrast to previous studies, the copolymer described here, apart from the substantial structural difference, shows a much higher molecular mass, and additionally, the biodegradability was

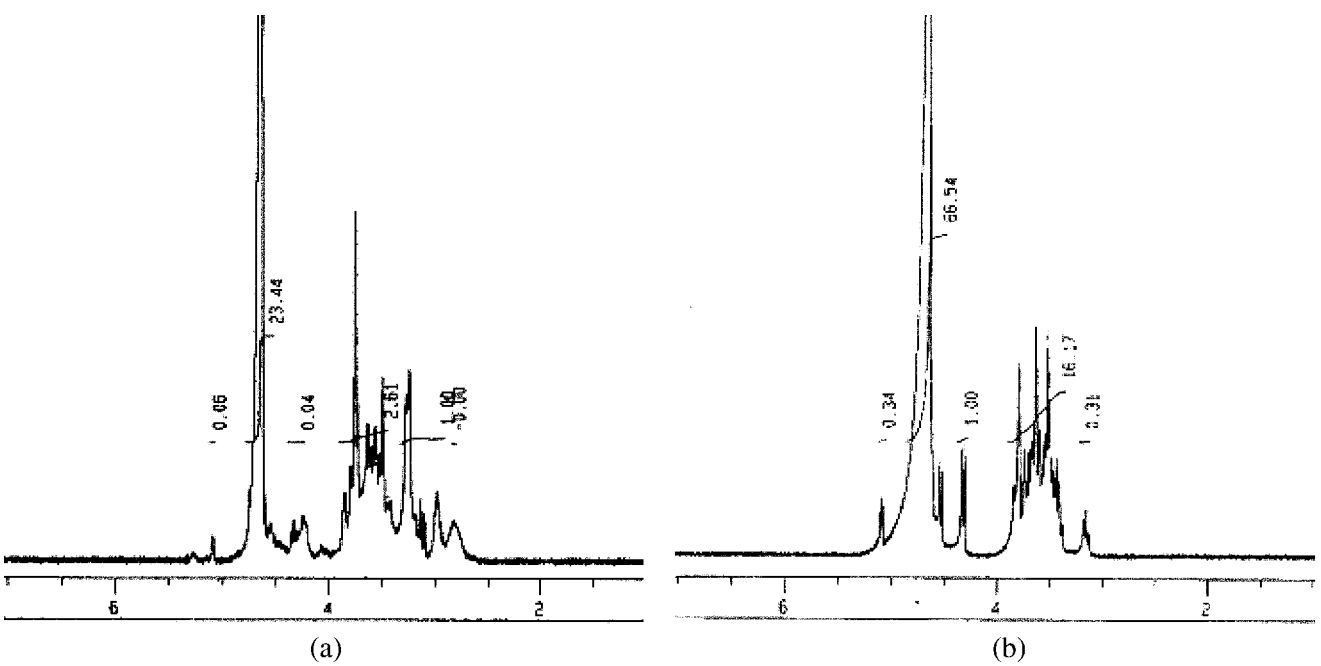


Figure 4 ^{1}H-NMR spectra of (a) poly(ethylenediaminetetra-acetic acid-*co*-lactose) (PEL) and (b) D-lactose (in D_2O).

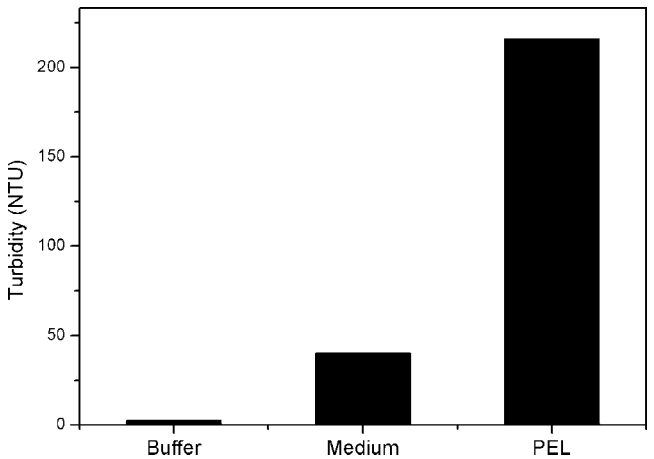


Figure 5 Turbidity of the microbe-inoculated solution of poly(ethylenediaminetetra-acetic acid-*co*-lactose) (PEL, **3**). Buffer was 0.1*M* potassium phosphate buffer (pH 7.2) at 25°C consisting of 71.7 mL of 1*M* K_2HPO_4 and 28.3 mL of 1*M* KH_2PO_4; medium: mineral medium solution. (NTU, nephelometric turbidity unit).

studied. The polyreaction was monitored using UV–vis spectroscopy to assess the optimum reaction time. After an initial steady increase, the absorption intensity reached a maximum after 96 h, and the reaction was stopped after 119 h (Fig. 2). That means it is recommendable to perform the polyreaction up to about 90 h to obtain an optimum yield and to avoid potential side-reactions. According to the determination of the carboxyl group content in PEL by titration using 0.05 NaOH, the functionality was found to be 1.88 mmol g^{-1}.

Spectroscopic characterization

The IR spectra of PEL, ethylenediaminetetra-acetic acid dianhydride (EDTA-DA), and lactose are shown in Figure 3. In the FTIR spectrum, new bands at 1744 and 1601 cm^{-1} appeared that can be ascribed to the C=O stretching vibration of the ester group and to the carboxylic groups of the EDTA moiety, respectively. Thus, the dianhydride group of EDTA-DA disappeared, and the ester bond appeared due to the polyreaction between EDTA-DA and lactose.

The ^{1}H-NMR spectra of lactose and PEL are shown in Figure 4. The spectrum of PEL [Fig. 4(a)] shows several new peaks such as at $\delta = 4.25$, $\delta = 3.24$, and $\delta = 2.82$, when compared with the spectrum of lactose. In the PEL, the broad peak at $\delta = 4.25$ ppm, looking like a merged peak, may be attributed to the —CH_2— protons of the ester bond [—C(=O)—O—C***H***$_2$—] between EDTA and lactose. The esterification of lactose with the EDTA dianhydride is expected to occur at the primary hydroxyl groups in the 6- and 6′-position of lactose, due to the generally higher reactivity and smaller steric hindrance of primary hydroxyl groups compared to secondary hydroxyl groups.[23–25] The highest peak at $\delta = 3.76$ ppm of PEL might stem from the —CH_2— of primary hydroxyl remaining after polymerization or possibly due to the esterification of secondary hydroxyls, while the —CH— proton signals might be merged to the broad peak at $\delta = 4.25$ ppm. The singlet at $\delta = 3.24$ corresponds to the —CH_2— protons of [—N(–)—C***H***$_2$—COOH]. The broad peak at $\delta = 2.82$ may be ascribed to the —CH_2— protons of [—N(–)—C***H***$_2$—C***H***$_2$—N(–)—].

Microbiological degradation

The copolymer PEL was degraded by a microbiological consortium consisting of a mixture of soil microbes and activated sludge. The suspension turbidity of the enriched mixed culture is shown in Figure 5. The turbidity of the microbe-enriched solution of polymer PEL was determined to 216 NTU (nephelometric turbidity unit), while the buffer and mineral solution shows 2.6 NTU and 40.1 NTU, respectively. This significant difference means indirectly that PEL is microbiologically degradable because the change of turbidity is due to the enrichment and growth of mixed culture. Therefore, it can be concluded that the copolymer can be degraded by the microbes under these conditions, which is indicated by the enhanced turbidity. Figure 6 indicates that PEL is microbiologically degradable exhibiting an induction phase of 5 days and an exponential phase of 2 days after induction.

Interestingly, our findings coincide with a very recent report, where nonpolymer-bound, uncomplexed EDTA and EDTA chelates with comparably low stability constants were found to be easily degraded by bacteria of the strain DSM 9103.[26] Also, the biodegradability of EDTA has been increasingly

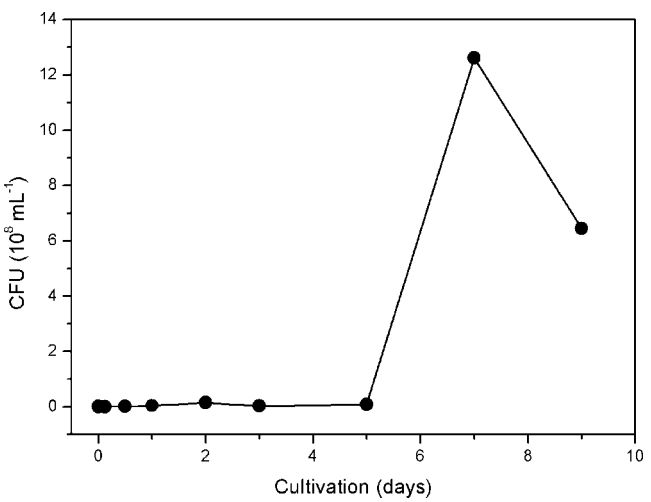


Figure 6 Microbiological degradation of poly(ethylenediaminetetra-acetic acid-*co*-lactose) based on colony-forming units (CFU) as a function of cultivation time.

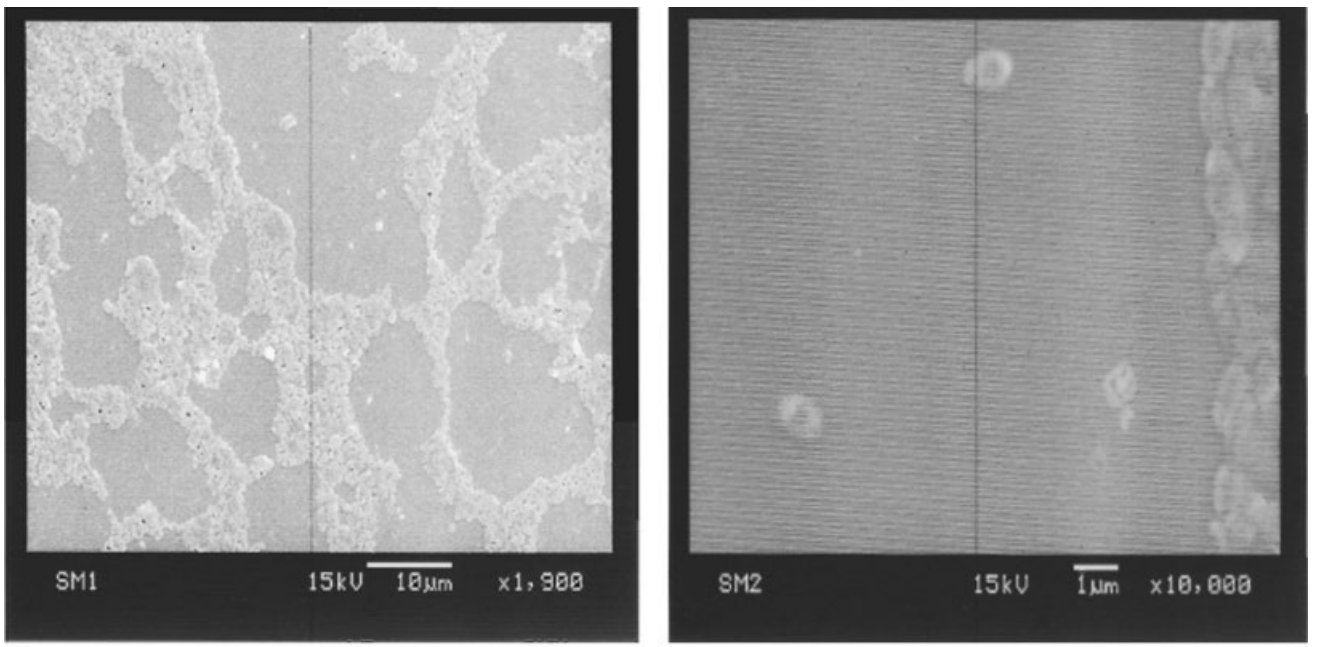


Figure 7 Scanning electron micrograph of the prominent microbial species in culture: (a) morphology of aggregated network (×1,900), (b) egg-shaped and cocci-shaped microbial species of the *Pseudomonas* type (×10,000).

recognized and investigated from different points of view such as the removal of heavy metals and remediation of sites contaminated with heavy metals or radionuclides.[25] With respect to metal chelates of EDTA, the complex EDTA-Fe(III) supported the growth of an *Agrobacterium* species[27] and also the degradation of the EDTA-Fe(III) was reported with the bacterial strain possibly belonging to the genus *Pseudomonas*.[28]

Lactose can be enzymatically degraded to a monosaccharide mixture, consumed by some strains of *Lactobacillus* and *Streptococcus*, and used to produce lactic acid by homofermentative lactic acid bacteria.[29] Thus, the microbiological degradability of PEL could be affected by these conditions. The morphological feature of the prominent culture for this degradation is shown in Figure 7. At 1900-fold magnification, an aggregated network [Fig. 7(a)] can be seen and at 10,000-fold magnification egg-shaped and cocci-shaped organisms of about 1–2 µm in length [Fig. 7(b)] can be discerned. The microorganism originating from the soil and the activated sludge, acclimating in an aerobic condition and the mineral medium, may be attributed to the *Pseudomonas* family.

Metal complexation studies

The metal complexing properties of the water-soluble PEL were investigated for 10 divalent and trivalent ions by the LPR.[3,27,28] This method yields retention profiles, which are plots of the retention R versus the filtration factor Z. The retention of metal ions in the cell solution by polymeric reagent can be calculated as follows:

$$R(\%) = c_r \times {c_0}^{-1} \times 100$$

where c_r is the metal concentration in the retentate (the cell solution after a filtrate volume of V_f has been passed) and c_o is the initial metal concentration in the cell.

Z is defined as the ratio of the volume of filtrate V_f and the volume of cell solution V_0:

$$Z = V_f \times {V_0}^{-1}$$

Typical retention profiles of PEL are shown in Figure 8. A polychelatogen concentration of 1 wt % in the cell solution was sufficient for quantitative complexation, as the polymer contained a large excess of complexing groups in comparison to the metal ion concentration (20 mg L^{-1}). The water-soluble polymer PEL showed a strong metal complexation with Cr(III) and Fe(III) with retention values of 100%, except for Co(II), Ni(II), Cu(II), Zn(II), Sr(III), Cd(II), Pb(II), and Al(III) with lower retention values (20–80%). Thus, the enrichment of Cr(III) and Fe(III) from the other metal ions can be achieved. The trend of retention values of Cu(II), when compared with those of Ni(II) and Co(II), are in accordance with those of other hydroxy group-containing polymers such as poly[(2-hydroxyethyl)-DL-aspartamide].[17]

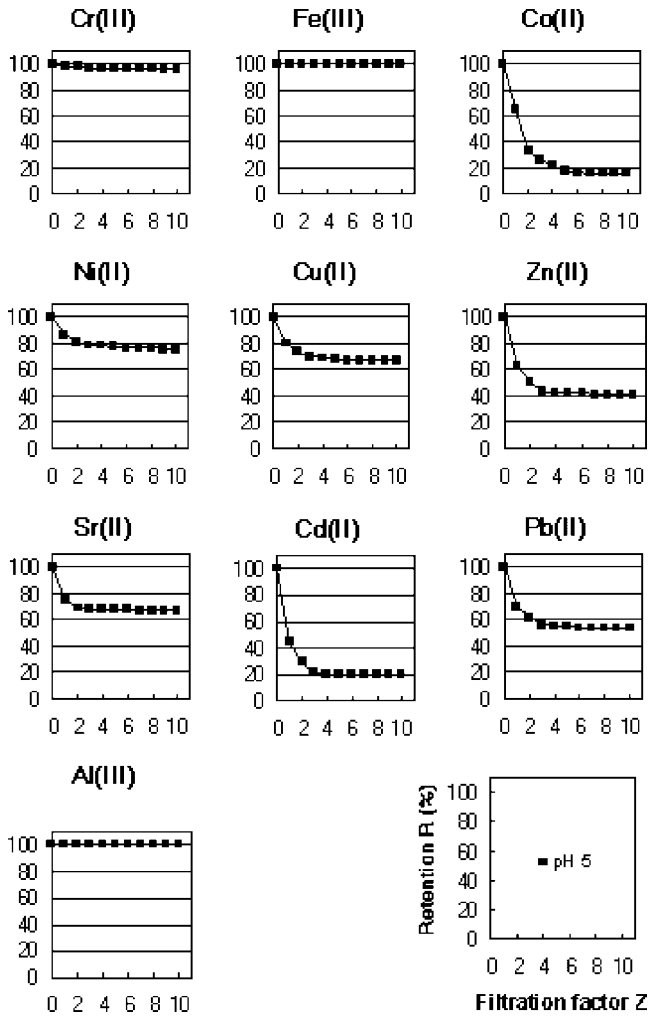


Figure 8 Retention profiles of poly(ethylenediaminetetra-acetic acid-*co*-lactose) **3** for 10 metal ions (1 wt %) at pH 5 using the liquid-phase polymer-based retention (LPR) method.

Thermogravimetric analysis

The thermal stability curves of the water-soluble PEL and its metal complex with Cu(II) (PEL-Cu) are shown in Figure 9. To assess the influence of the metal on the degradation pattern of the functional moieties, the copper-saturated polymer–metal complex was also prepared. In the case of the uncomplexed polymer,

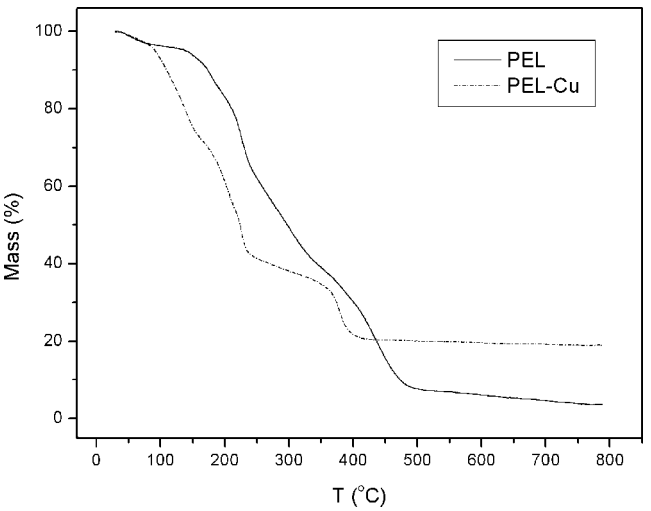


Figure 9 Thermogravimetric analysis of poly(ethylenediaminetetra-acetic acid-*co*-lactose) (PEL, **3**) and its Cu(II) complex (PEL-Cu).

the typical mass loss was observed at 140°C, and the mass loss reached 20% at 435°C, but PEL-Cu showed a much complicated degradation pattern from 80°C to 435°C, which represents no further noticeable mass loss with a 20% remainder. The metal binding value of PEL for copper was found to be 182 mg g^{-1} polymer.

By kinetic analysis of the decomposition of PEL and its copper complex (PEL-Cu), the activation energy (E), frequency factor (A), and entropy of activation (S) for the thermal decomposition were evaluated from the computational analysis of the TGA data, using several integral models as described in the experimental section. The kinetic parameters such as the activation energy, the frequency factor, and the entropy of activation for thermal degradation are summarized (Table I). The PEL-Cu complex shows a slightly lower activation energy than PEL, even though there is a small variation for each model. From this difference in activation energy, it can be concluded that the polymer–metal complex was slightly less stable than polymer. The thermal stability of polymer–metal complexes is known to be affected primarily by the nature of the polymer main-chain and microenvironmental conditions such as additional coordination bonds and crosslinking. It is

TABLE I
Kinetic Parameters for the Thermal Decomposition of Poly(ethylenediaminetetra-acetic acid-*co*-lactose) (PEL) and Its Cu(II) Complex (PEL-Cu)

Sample	T_{max} (K)	Method	E_a (kJ mol^{-1})	A (s^{-1})	ΔS (J K^{-1} mol^{-1})
PEL	503.15	CR	47.7	74.2	−214.3
		VK	24.6	3.8	−239.1
		BR	28.7	7.8	−233.1
PEL-Cu	500.15	CR	18.4	2.3	−243.1
		VK	22.7	8.3	−232.5
		BR	26.5	24.4	−223.5

CR, Coats–Redfern; VK, van Krevelen; BR, Broido.

known that the thermal stability of functional polymers with metal will be enhanced.[30–32] However, on the other hand, some recent reports support our TGA results.[33] As the polymer interacts with metal ions, the thermal energy supplied to the polymer–metal complex may result in a catalytic role of metal ion to the thermal decomposition of the polymer–metal complex.

CONCLUSIONS

The polycondensation of ethylenediaminetetra-acetic acid dianhydride and D-lactose can be conveniently performed in an one-pot reaction, yielding a copolymer with a molecular mass of 132 kg mol^{-1} after a reaction time of 119 h. The content of pendant carboxylic groups of the copolymer was determined by titration and found to be 1.88 mmol g^{-1} polymer. Conventional microbiological studies showed that the copolymer is microbiologically degradable. In metal-complexing studies, Cr(III) and Fe(III) were found to bind strongly to the polymer with retention values of 100%. By thermogravimetric analysis of the polymer and its polymer–copper complex, the polymer showed a slightly higher thermal stability than the polymer–metal complex. The maximum binding capacity of PEL for copper was determined to be 182 mg g^{-1} polymer.

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