Synthesis and Properties of Hydrophilic Polymers. IX. Synthesis, Biodegradability, and Metal Complexation of Copolymers of Ethylenediaminetetraacetic Acid Dianhydride and Lactose

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Received 26 March 2001; accepted 6 January 2003

ABSTRACT: The synthesis and characterization of poly(ethylenediaminetetraacetic acid-*co*-lactose) with pendant carboxylic groups of high molar mass (132 kg mol^{-1}) is described. The polycondensate was hydrolytically and microbiologically degradable with 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 with the liquid-phase polymer-based retention (LPR) method. In addition, the complexing capacity of the Cu(II)-saturated copolymer was determined by thermogravimetric analysis to be 182 mg g^{-1} of polymer. According to the retention profiles determined as a function of the filtration factor with LPR in conjunction with inductively coupled plasma spectrometry, Cr(III) and Fe(III) showed a strong interaction with this polymer under these conditions, as indicated by retention values of about 100% at pH 5. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 650–657, 2003

Key words: biodegradable; metal–polymer complexes

INTRODUCTION

The incorporation of chelating ligands into polymers via condensation polymerization is well known as the earliest method for the formation of chelate-forming polymers. Prime examples have included polymers formed by the condensation of formaldehyde with reactive phenols or amines.[1–4] Other types include 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] with a number of organic ligands containing aminoacetic 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 EDTA and diethylenetriaminepentaacetic acid (DPTA), which represent promising candidates for the preparation of environmentally degradable polycondensates, were reported.[7]

During recent decades, the separation and enrichment of hazardous metal ions in aqueous solutions have played an important role in their removal from municipal and industrial wastewater. Among the 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] However, 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 have disadvantages, including reactions in the 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 and 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 analytical and technical scales.

A variety of soluble polymers, including derivatives of poly(ethylenimine),[13] poly(vinylamine),[14] poly(acrylic acid-*co*-acryl amide),[15] polychelatogens based on polyurethanes, poly(vinyl alcohol), and other co-

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Journal of Applied Polymer Science, Vol. 90, 650–657 (2003)

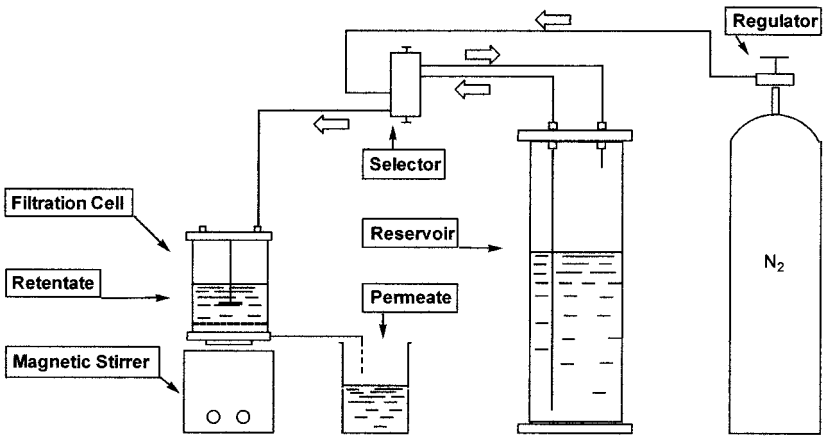


Figure 1 Experimental setup of the membrane filtration system for the complexation studies in aqueous solution with the LPR technique.

polymers, have been studied for homogeneous-phase applications. Previously, we investigated hydroxy-functional polymers based on aziridine, showing that poly[1-(2-hydroxyethyl) aziridine] containing hydroxyl groups in the side chain were able to bind a number of metal ions.[16] Our other recent studies include the synthesis of environmentally degradable chelating polymers based on EDTA[7] and on aspartic acid, such as poly[(2-hydroxyethyl)-DL-aspartamide].[17]

In this study, we report on the polycondensation, characterization, and microbiological degradation of a copolymer of ethylenediaminetetraacetic acid dianhydride (EDTA-DA) and lactose and also on its metal-complexing properties.

EXPERIMENTAL

Materials

EDTA-DA (Aldrich, 98%) and D-lactose (Sigma, minimum 99%) were used after being dried at 60°C *in vacuo*, and formamide (Aldrich, 99+%) was dried before use. All metal salts were used in the form of nitrates and purchased from Junsei, except Ni(II) (Aldrich), Cr(III) (Janssen), and Pb(II) and Sr(II) (Yakuri). K_2HPO_4 (Aldrich, 98+%), KH_2PO_4 [Oriental Chemical Industry (OCI), + extrapure], $(NH_4)_2SO_4$ (OCI, extrapure), $MgSO_4 \cdot 7H_2O$ (OCI, extrapure), dextrose (OCI, anhydrous), Bacto-agar (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 a 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 of distilled water].

Instruments and methods

Fourier transform infrared (FTIR) spectra (KBr pellets) were recorded on a PerkinElmer 2000 series and ^{1}H-NMR spectra were recorded on a Jeol JNM-LA 300 WB Fourier transform NMR spectrometer (300 MHz). Molecular masses were measured by light-scattering measurements (Malvern 4700C). Thermal gravimetric analysis was performed with a TGA 2050 instrument (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); an autoclave (Auto Clave DAC 811) and a clean bench (DVB 912, 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 a suspending ball level (Schott–Geraete) was used. Carboxyl groups were determined with a titrator (Metrohm 702 SM Titrino).

Membrane filtration was carried out with a system described previously.[11,12,18] The membrane filtration unit consisted of a membrane filtration cell, which contained the polymer solution and 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 the decomposition of the polymers and the polymer–metal complexes, the following models were used: the Coats–Redfern[19] model

$$\ln\frac{f(\alpha)}{T^2} = \ln\left[\frac{AR}{\beta E_a}\left(1 - 2\frac{RT}{E_a}\right)\right] - \frac{E_a}{RT} \quad (1)$$

the Van Krevelen[20] model

$$\ln f(\alpha) = \ln\left[\frac{A}{\beta}\left(\frac{0.368}{T_{\max}}\right)^{E_a/RT_{\max}}\left(\frac{E_a}{RT_{\max}} + 1\right)^{-1}\right] + \left(\frac{E_a}{RT_{\max}} + 1\right)\ln T \quad (2)$$

and the Broido[21] model

$$\ln f(\alpha) = \ln\left[\frac{AR}{\beta E_a}T^2{}_{\max}\right] - \frac{R}{E_a} \times \frac{1}{T}$$

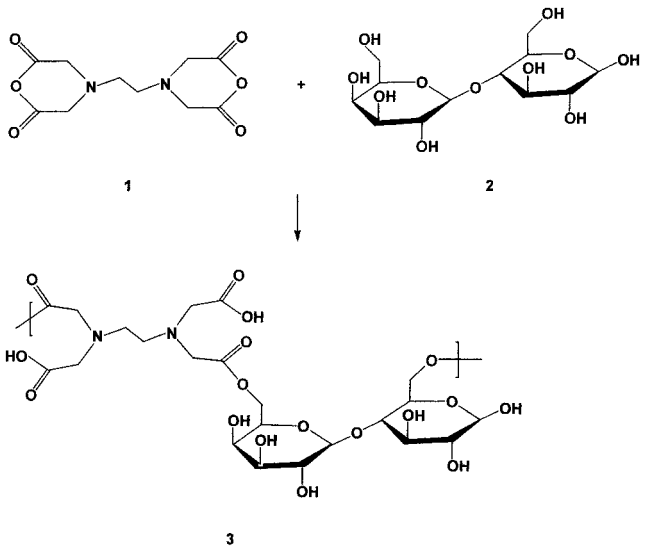
where α is the ratio of actual weight loss to total weight loss corresponding to the degradation process and is equal to $(W_0 - W)/(W_0 - W_f)$, where W_0 is the initial weight, W is the weight at temperature T, and W_f is the final weight; $f(\alpha)$ is a function of α; β is the heating rate (° $\min^{-1}$); $T_{\max}$ is the temperature of the maximum rate of weight loss (K); E_a is the activation energy (kJ); and A is the frequency factor (s^{-1}). The entropy of activation (ΔS) was calculated from the equation $A = (kT_{\max}h^{-1})(e^{\Delta S/R})$, where k is Boltzmann's constant, h is Planck's constant, and R is the gas constant.

Synthesis of poly(ethylenediaminetetraacetic acid-*co*-lactose) (PEL)

D-Lactose (1.130 g, 3.3 mmol) was dissolved in 10 mL of freshly dried formamide, and a suspension of 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 ultraviolet (UV) monitoring. During the polyreaction, the suspension changed to a clear, transparent, and slightly yellow liquid after 27 h. When it reached a maximum absorbance during UV monitoring, the mixture was cooled and precipitated into ethanol with a 10-fold excess. After the precipitation, the polymer was filtered and dried with a rotary evaporator. The product was then dissolved in 70 mL of water, neutralized with 0.1*M* sodium hydroxide, and freeze-dried to a white solid after purification by membrane filtration (Amicon YM1 membrane, nominal molar mass exclusion limit = 1 kg mol^{-1}). The yield was 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 with 0.05*N* NaOH.



Scheme 1 Polyreaction of EDTA-DA (**1**) and D-lactose (**2**), yielding PEL (**3**).

Microbiological degradation of PEL

Enrichment and isolation

A mixed culture was collected from the soil of the Kwangju Institute of Science and Technology campus at the ground surface and a 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 of PEL in 150 mL of solution (the ratio of mineral medium to phosphate buffer was 1:2). For microbiological enrichment, the mixed culture was acclimated to the polymer solution at a constant temperature (25°C) under stirring.

Batch test for polymer degradation

A solid medium for colony-forming unit (CFU) enumeration was prepared as the first step with a solution of 100 mg of polymer and 40 mg of Agar (4 wt %) in 1 L of phosphate buffer (pH 7.2); this was 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 % phosphate buffer), and then, the inoculated solution was stirred at 25°C. To monitor the degradation process on the basis of microbial growth, 100-μL aliquots were collected from the inoculated solution, diluted 10-fold to test tubes, and

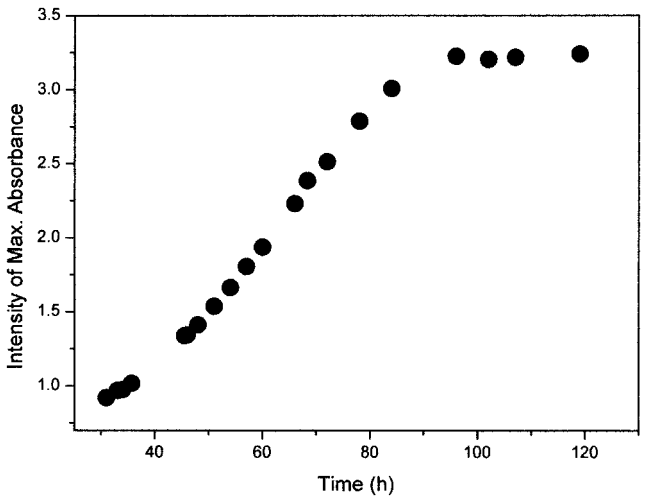


Figure 2 UV monitoring of the reaction time for the polyreaction of EDTA-DA and D-lactose.

spread on the solid medium. Then, the CFUs were counted and assessed as an indicator of degradability. Each test was done twice.

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 concentration of each metal ion of 20 mg L^{-1}. The pH of the cell and the reservoir solutions were adjusted to 5, and the system was pressurized with N_2. A membrane with a nominal molar mass cutoff of 1 kg mol^{-1} (Amicon YM1) was used. The filtrate fractions (Z = 1–10) were collected and subjected to analysis by ICP.

For the thermal stability studies of metal-saturated samples by thermogravimetric analysis (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 EDTA-DA and lactose in formamide. The molecular mass was found to be 132 kg mol^{-1} by light-scattering measurements after the removal of low-molecular constituents from the higher molecular mass fractions (>1 kg mol^{-1}) by membrane filtration. The incorporation of iminodiacetic acid derivatives such as EDTA and DPTA can produce chelate-forming polymers able to bind many multivalent metals.[1,22] Water-soluble, carboxy-functional polyesters based on poly(ethylene glycol) with EDTA or DPTA incorporated into the polymer backbone have been described.[7] In contrast to previous studies, the copolymer described here showed a much higher molecular mass, and additionally, biodegradability was studied. The polyreaction was monitored with UV–visible spectroscopy to assess the required reaction time. The intensity reached a maximum after 96 h, and the reaction was stopped after 119 h (Fig. 2). According to the determination of the carboxyl group content in PEL by titration with 0.05*N* NaOH, the functionality was 1.88 mmol g^{-1}.

Spectroscopic characterization

The IR spectra of PEL, EDTA-DA, and lactose are shown in Figure 3. The strong bands at 1813 and 1763 cm^{-1} were assigned to the anhydride moieties of EDTA-DA. In the spectrum of PEL, the new band at 1744 cm^{-1} was ascribed to the C═O stretching vibration of the ester group, and the band at 1601 cm^{-1} was assigned to the carboxylic groups of the EDTA moiety. Thus, the dianhydride group of EDTA-DA disappeared, and the ester bond appeared as the polyreaction occurred 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)] showed several new peaks, including at δ = 4.25, 3.24, and 2.82 ppm, compared to the spectrum of lactose. In PEL, the broad peak at δ = 4.25 ppm, looking like a merged peak, was attributed to the —CH_2— protons of the ester bond [—C(═O)—O—CH_2—] between EDTA and lactose. The esterification of lactose with the EDTA dianhydride was expected to occur at the primary hydroxyl groups in the 6 and 6′ positions of lactose, due to the generally higher reactivity and smaller steric hindrance of primary hydroxyl groups compared to secondary hydroxyl groups.[23–25] The

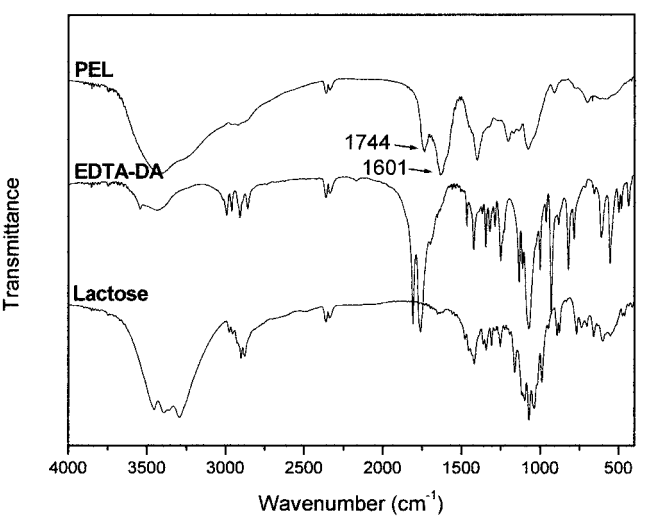


Figure 3 FTIR spectra of (a) PEL, (b) EDTA-DA, and (c) D-lactose.

highest peak, at δ = 3.76 ppm, of PEL might have stemmed from the —CH_2— of the primary hydroxyl remaining after polymerization or might possibly have been due to the esterification of secondary hydroxyls, whereas the —CH— proton signals might have merged to the broad peak at δ = 4.25 ppm. The singlet at δ = 3.24 ppm corresponded to the —CH_2— protons of [—N(—)—CH_2—COOH]. The broad peak at δ = 2.82 ppm was ascribed to the —CH_2— protons of [—N(—)—CH_2—CH_2—N(—)—].

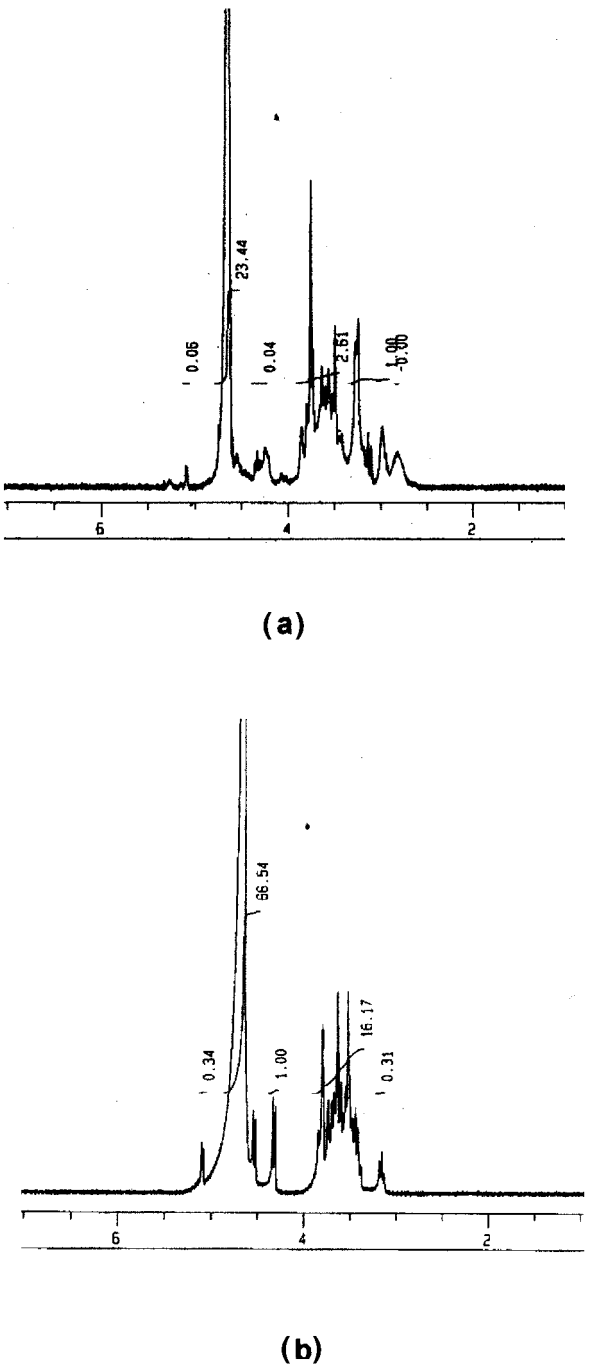


Figure 4 ^{1}H-NMR spectra of (a) PEL and (b) D-lactose (in D_2O).

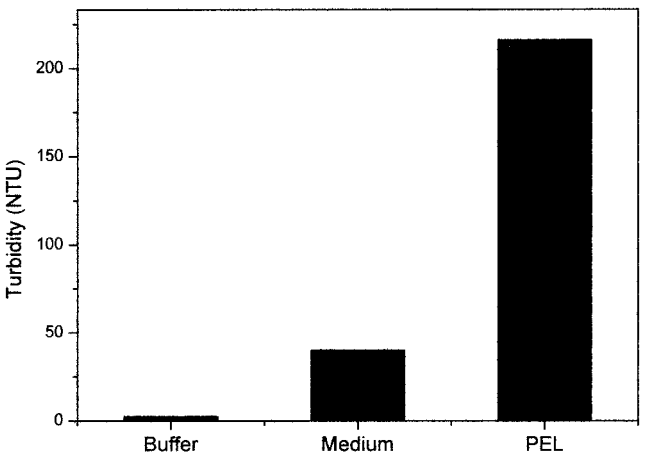


Figure 5 Turbidity of the microbe-inoculated solution of PEL (**3**). The buffer was 0.1*M* potassium phosphate buffer (pH = 7.2) at 25°C, consisting of 71.7 mL of 1*M* K_2HPO_4 and 28.3 mL of 1*M* KH_2PO_4. The medium was a mineral medium solution.

Microbiological degradation

The copolymer PEL was allowed to be 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 PEL was 216 nephelometric turbidity units (NTU), whereas those of the buffer and mineral solution were 2.6 and 40.1 NTU, respectively. This difference meant indirectly that PEL was microbiologically degradable because the change of turbidity was due to the enrichment and growth of the mixed culture. Figure 6 indicates that PEL was microbiologically degradable, exhibiting an induction phase of 5 days and an exponential phase of 2 days after induction, whereas

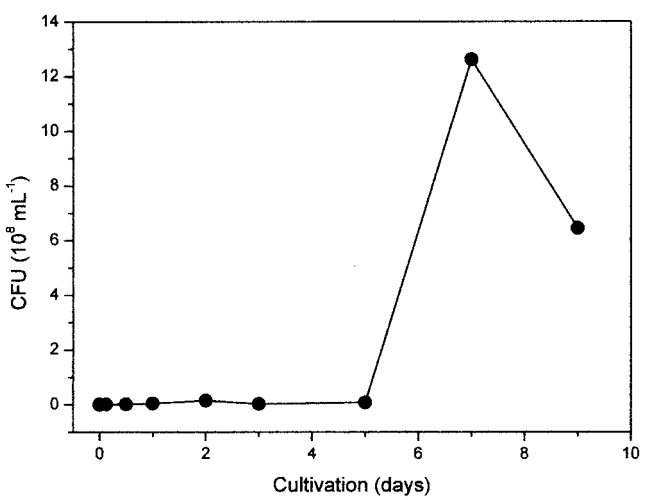


Figure 6 Microbiological degradation of PEL on the basis of CFUs as a function of cultivation time.

the control test with PEL absent showed almost no change with nearly zero CFUs compared to PEL.

Interestingly, our findings coincided with a very recent report where 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 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 EDTA–Fe(III) was reported with a 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 can be 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 features of the prominent culture for this degradation is shown in Figure 7. At 1900× magnification, an aggregated network [Fig. 7(a)] can be seen, and at 10,000× magnification, egg-shaped and cocci-shaped organisms about 1–2 μm in length [Fig. 7(b)] could be discerned. The microorganism originating from the soil and the activated sludge, acclimating in aerobic conditions and the mineral medium, could have been from the *Pseudomonas* family.

Metal-complexation studies

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

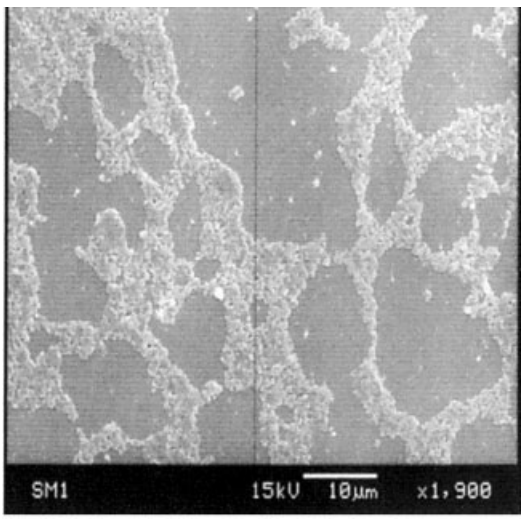
$$R\ (\%) = C_r \times C_0^{-1} \times 100$$

where c_r is the metal concentration in the retentate [the cell solution after a filtrate volume (V_f) has been passed] and c_0 is the initial metal concentration in the cell.

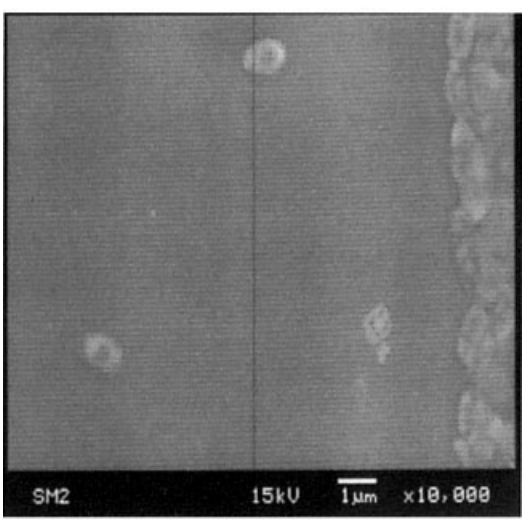
Z is defined as the ratio of V_f to the volume of cell solution (V_0):

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

The 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 was achieved. The trend of retention values of Cu(II) compared to Ni(II) and Co(II) were in accordance with those of other hydroxy groups of poly[(2-hydroxyethyl)-DL-aspartamide].[17]



(a)



(b)

Figure 7 Scanning electron micrograph of the prominent microbial species in culture: (a) morphology of the aggregated network (1900×) and (b) egg-shaped and cocci-shaped microbial species of the *Pseudomonas* type (10,000×).

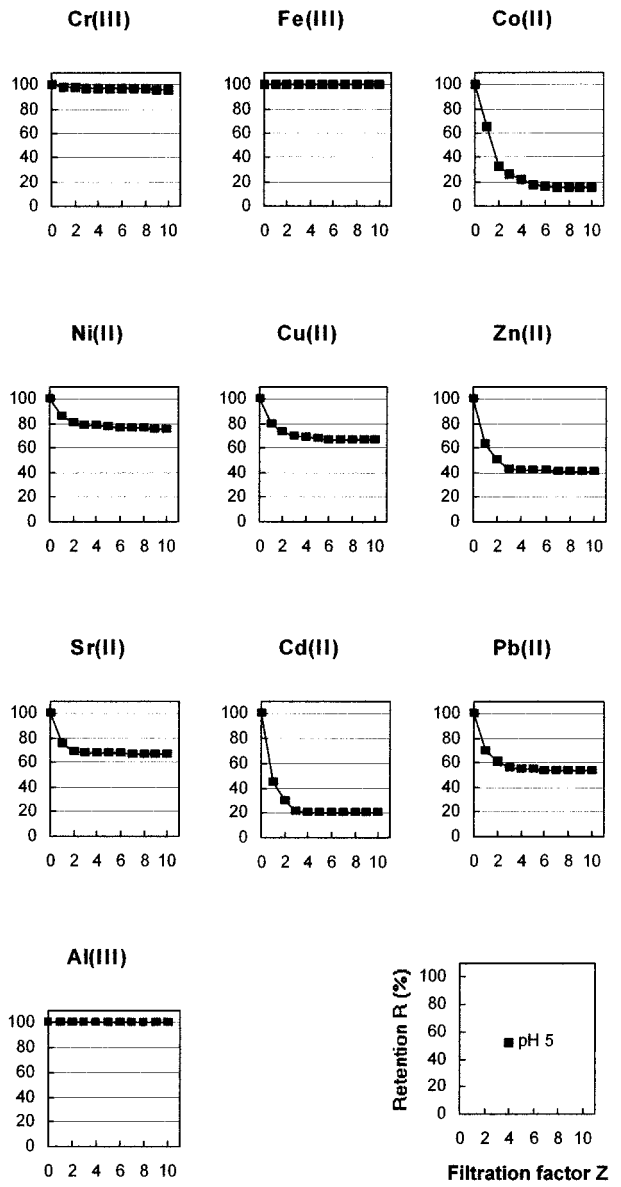


Figure 8 Retention profiles of PEL (**3**): 1 wt % for 10 metal ions at pH 5 with the LPR method.

TGA

The thermal stability curves for 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, we prepared the Cu-saturated polymer–metal complex. In case of the uncomplexed polymer, the typical mass loss was observed at 140°C, and the mass loss reached 20% at 435°C, but PEL–Cu showed a very complicated degradation pattern from 80 to 435°C, which represented no further noticeable mass loss with a 20% remainder. A metal-binding value of PEL for copper of 182 mg g^{-1} polymer was thus determined.

By kinetic analysis of the decomposition of PEL and its copper complex (PEL–Cu), E_a, A, and ΔS for the thermal decomposition were evaluated from the computational analysis of the TGA data with several integral models as described in the Experimental section. The kinetic parameters, including E_a, A, and ΔS, for thermal degradation are summarized in Table I. The PEL–Cu complex showed a slightly lower E_a than PEL, even though there was a small variation for each model. From this difference in E_a, we concluded that the polymer–metal complex was slightly less stable than the 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 known that the thermal stability of functional polymers with metal will be enhanced.[32–34] However, however, some recent reports support our TGA results.[33,34] As the polymer interacts with metal ions, the thermal energy supplied to the polymer–metal complex may result in a catalytic role of the metal ion to the thermal decomposition of the polymer–metal complex.

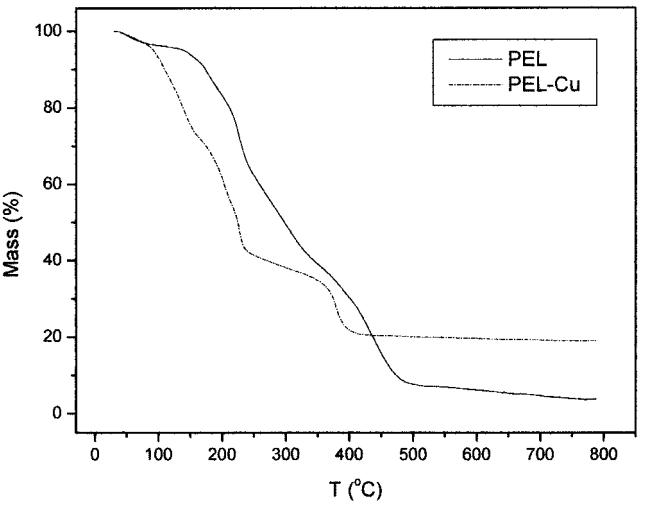


Figure 9 TGA of PEL (**3**) and PEL–Cu.

CONCLUSIONS

The polycondensation of EDTA-DA and D-lactose was conveniently performed in an one-pot reaction and

TABLE I
Kinetic Parameters for the Thermal Decomposition of PEL and PEL–Cu

Sample	T_{max} (K)	Method	E_a (kJ mol^{-1})	A (s^{-1})	ΔS (JK^{-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; VR = Van Krevelen; BR = Broido.

yielded a copolymer with a molecular mass of 132 kg mol^{-1} after a reaction time of 19 h. The content of pendant carboxylic groups of the copolymer were determined by titration and were 1.88 mmol g^{-1} of polymer. Conventional microbiological studies showed that the copolymer was microbiologically degradable. In metal-complexing studies, Cr(III) and Fe(III) bound strongly to the polymer with retention values of 100%. In TGA 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 182 mg g^{-1} of polymer.

References

1. Hodgkin, J. H. In Encyclopedia of Polymer Science and Engineering, 2nd ed.; Kroschwitz, J. I., Ed.; Wiley: New York, 1989; Vol. 3.
2. Parrish, J. R. Chem Ind 1955, 387.
3. Gregor, H. P.; Taifer, M.; Citarel, L.; Becker, E. I. Ind Eng Chem 1952, 44, 2843.
4. Pennington, L. D.; Williams, M. B. Ind Eng Chem 1959, 51, 759.
5. Ueda, M.; Hazome, H.; Imai, Y. Kobunshi Ronbunshu Eng Ed 1975, 4, 287.
6. Schwarzenbach, G.; Kampitsch, E.; Steiner, R. Helv Chim Acta 1945, 28, 1133.
7. Tuelue, M.; Geckeler, K. E. Polym Int 1999, 48, 909.
8. Scott, K. Membrane Separation Technology: Industrial Applications and Markets; Scientific and Technical Information: Oxford, England, 1990.
9. Geckeler, K. E.; Volchek, K. Environ Sci Technol 1996, 30, 725.
10. Spivakov, B. Y.; Geckeler, K. E.; Bayer, E. Nature 1985, 315, 313.
11. Geckeler, K. E.; Bayer, E.; Spivakov, B. Y.; Shkinev, V. M.; Vorobeva, G. A. Anal Chim Acta 1986, 189, 285.
12. Geckeler, K. E.; Shkinev, V. M.; Spivakov, B. Y. Sep Purif Methods 1988, 17,105.
13. Rivas, B. L.; Geckeler, K. E. Adv Polym Sci 1992, 102, 171.
14. Geckeler, K. E.; Lange, G.; Eberhardt, H.; Bayer, E. Pure Appl Chem 1980, 52, 1883.
15. Rivas, B. L.; Pooley, S. A.; Soto, M.; Geckeler, K. E. J Polym Sci Part A: Polym Chem 1997, 35, 2461.
16. Geckeler, K. E.; Rivas, B. L.; Zhou, R. Angew Makromol Chem 1991, 193, 195.
17. Choi, S. J.; Geckeler, K. E. Polym Int 2000, 49, 1519.
18. Geckeler, K. E. In Polymeric Materials Encyclopedia; CRC: Boca Raton, FL, 1996; Vol. 6, p 4101.
19. Coats, A. W.; Redfern, J. P. J Polym Sci Part B: Polym Lett 1965, 3, 921.
20. Van Krevelen, D. W.; Van Heerden, C.; Humfjens, F. J. Fuel 1951, 30, 253.
21. Broido, A. J Polym Sci Part A-2: Polym Phys 1969, 7, 1761.
22. Noertemann, B. Appl Microbiol Biotechnol 1999, 51, 751.
23. Martin, B. D.; Linhardt, R. J.; Dordick, J. S. Biomaterials 1998, 19, 69.
24. Drummond, C. J.; Wells, D. Colloids Surf A 1998, 141, 131.
25. Gao, C.; Whitecombe, M. J.; Vulfson, E. N. Enzyme Microb Technol 1999, 25, 264.
26. Satroutdinov, A. D.; Dedyukhina, E. G.; Chistyakova, T. I.; Witschel, M.; Mindevich, I. G.; Eroshin, V. K.; Egli, T. Environ Sci Technol 2000, 34, 9.
27. Lauff, J. J.; Steele, D. B.; Coogan, L. A.; Breitfeller, J. M. Appl Environ Microbiol 1990, 56, 3346.
28. Miyazi, H.; Suzuki, S.; Imada, K. Environ Sci 1997, 10, 257.
29. Venkatesh, K. V. Process Biochem 1998, 33, 483.
30. Kaliyappan, T.; Swaminathan, C. S.; Kannan, P. Polymer 1996, 37, 2865.
31. Kaliyappan, T.; Kannan, P. J Polym Sci Part A: Polym Chem 1996, 34, 3551.
32. Bajpai, A.; Rai, S. J Polym Sci 1877, 69, 751.
33. Oriol, L.; Alonso, P. J.; Martineoz, J. I.; Pinol, M.; Serrano, J. L. Macromolecules 1994, 27, 1869.
34. Samal, S.; Das, R. R.; Sahoo, D.; Acharya, S. Polym Int 1997, 44, 41.