

The Synthesis and Characterization of Novel Carboxyl Telechelic Microspheres

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ABSTRACT: A series of novel carboxyl telechelic microspheres (CTMs) with different length of oligo-caprolactone telechelic chains are readily prepared via a three-step approach involving: (1) the hydrolytic oligomerization of ϵ -caprolactone, (2) the esterification of oligo-caprolactone with maleic anhydride, and (3) the suspension polymerization of maleic acid polycaprolactone ester acid (MAPCLA) with divinylbenzene. The CTMs, which are water swellable, spherical, and porous, contain carboxyl functionalities of 1.0 to 4.2 mEq/g (dry), which are found to be lower swelling change (during conversion of ionic form) and higher exchange efficiencies than those of the Emerk. IV resin.

The intermediate products, oligo-caprolactone, and MAPCLA are characterized by the acid–base titration, hydroxyl value titration, and infrared and ^1H nuclear magnetic resonance analysis, respectively. The morphology and porous of CTMs are also tested by scanning electron microscopy and Brunauer-Emmett-Teller technology. The effects of the length of the telechelic chains and the degree of crosslinking (divinylbenzene), as well as the amount of porogen (toluene), on the physical and chemical parameters of the CTMs are also described. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 68: 205–216, 1998

Key words: ϵ -caprolactone; telechelic; microsphere; ion-exchange resin

INTRODUCTION

Ion exchange resins have been widely used for water treatment, sugar purification, analytical chemistry and chromatography, catalysis, hydrometallurgy, pharmaceuticals, and medical applications.^{1–6} But all of the available resins have the identical structure; that is, their pendent groups are very short in length and attached to a cross-linked hydrophobic backbone.⁷ This unique structure usually has a few shortcomings, as follows: (1) lower exchange efficiency and (2) higher volume change ratio, while the resins converse from one ionic form to another (as in normal exhaustion and regeneration cycles).

For practical applications, the resins with higher exchange efficiency and lower volume change ratio are needed. Therefore, a series of novel resins with different length of oligo-caprolactone branch chains in the molecular structure (as shown in Fig. 1) were designed. These novel resins have two different kinds of carboxyl groups, one of which is close to the backbone, and another terminal carboxyl group is attached to the backbone via a long oligo-caprolactone pendent chain, and are defined as the carboxyl telechelic microspheres (CTMs) in this article because the oligo-caprolactone branch chains have some of hydrophilicity (or biocompatibility) and can readily rotate or stretch in wet. Consequently, these CTMs may present excellent properties for the purposes of ion exchange and separation, as well as bioengineering applications.

The synthesis includes three main reactions. These are (1) the ring opening oligomerization of

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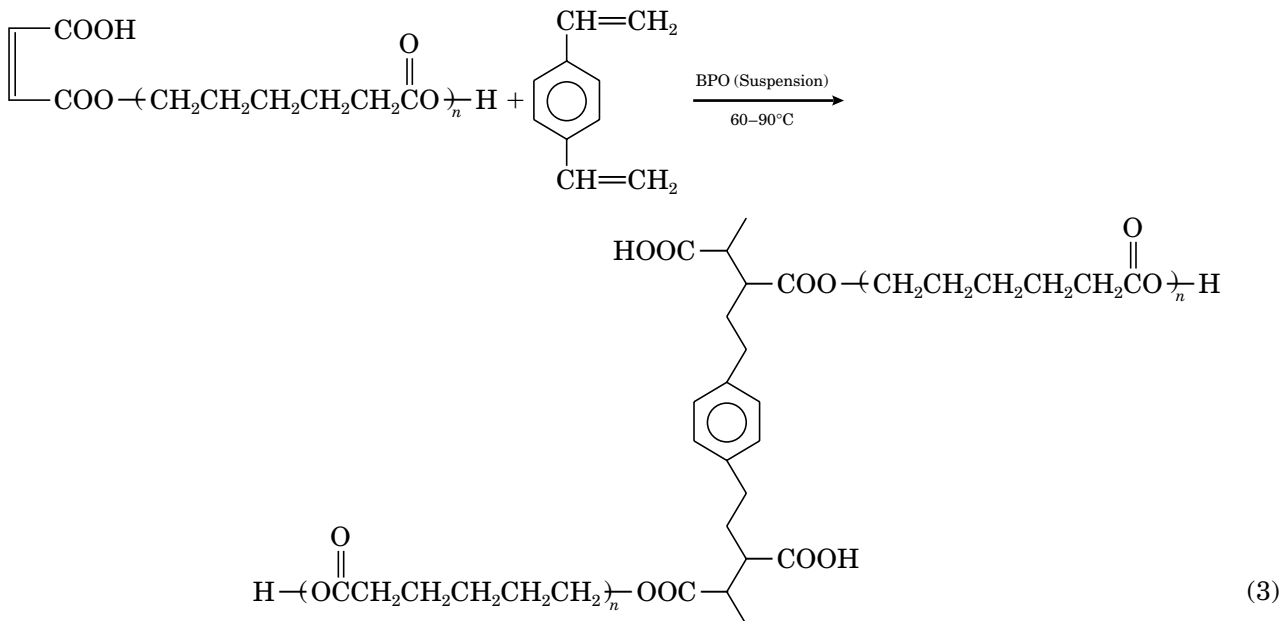
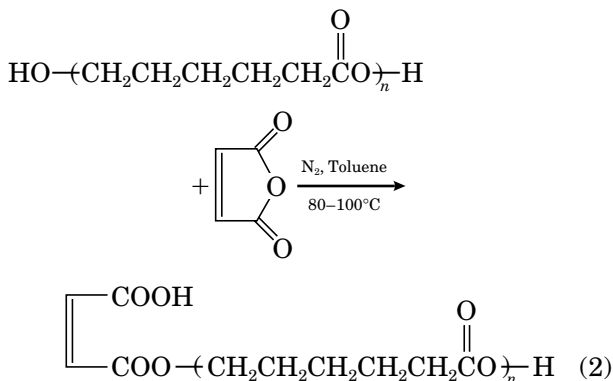
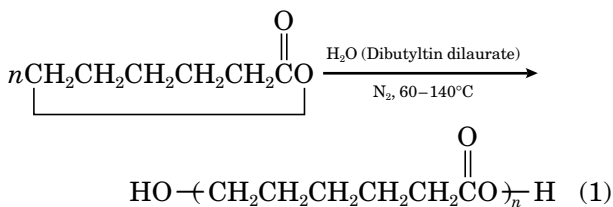
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caprolactone initiated by water and catalyzed with dibutyltin dilaurate [see eq. (1)], (2) the esterification of oligo-caprolactone with maleic anhydride [see eq. (2)], and (3) the suspension polymerization of maleic acid polycaprolactone ester acid (MAPCLA) with divinylbenzene [see eq. (3)].



This article concentrates on the synthesis and characterization of the CTMs. The physical parameters (carboxyl functionality, water swellability, and pore distribution) and the exchange properties of the CTMs are also discussed.

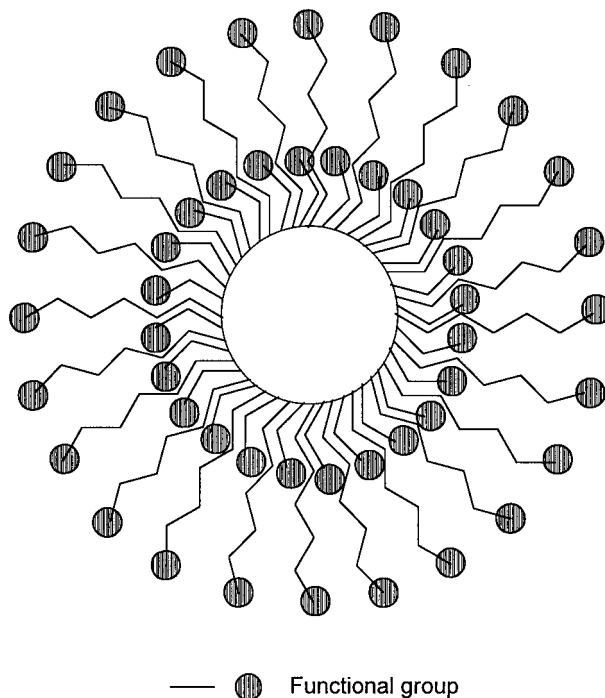


Figure 1 The schematic model of carboxyl telechelic microsphere (CTM).

EXPERIMENTAL

The Hydrolytic Oligomerization of ϵ -Caprolactone

ϵ -Caprolactone (Aldrich) was distilled under reduced pressure (about 5 mm Hg) before use. Dibu-

Table I Oligomerizations of ϵ -Caprolactone Initiated with Water and Catalyzed with Dibutyltin Dilaurate

Series	Cat. (Mol % Monomer)	Water (Mol % Monomer)	Initiating Efficiency of Water (%)	Molecular Weight		
				By ABT ^a	By HVT ^b	By NMR
A	0.25	280	17.9	245	218	236
B	0.25	180	16.3	407	—	—
C	0.25	160	15.5	478	470	—
D	0.25	140	16.6	508	—	—
E	0.25	80	16.1	902	935	—
F	0.25	50	18.7	1236	—	—

^a ABT, acid-base titration.^b HVT, hydroxyl value titration.

tyltin dilaurate (Aldrich) was used as received. Polymerization [as in eq. (1)] was performed in bulk in a flask with a ball condenser. The reaction mixture was exhausted via two successive cycles and protected with nitrogen. The polymerization flask was equipped with a magnetic stirrer and heated by silicone oil. The polymerization was controlled at 60–90°C for 3–6 h, then 130–140°C for 6–10 h. At the end of reaction, the reaction mixture was dissolved in acetone and precipitated into water, then filtered and dried under vacuum at 60°C. The samples were characterized by titration and infrared (IR) and ¹H nuclear magnetic resonance (¹H-NMR) measurement; the results are shown in Table 1 and Figures 4 and 5, respectively.

The Synthesis of Maleic Acid Polycaprolactone Ester Acid (MAPCLA)

The reaction [as in eq. (2)] proceeded under nitrogen protection in a flask with a ball condenser and a magnetic stirrer. ϵ -Caprolactone oligomer

was mixed with a 150% molar excess of the stoichiometric amount of maleic anhydride. After reaction at 80–100°C for 14 h, the product mixture was sublimed under reduced pressure and nitrogen purging to remove the unreacted maleic anhydride, then dissolved in acetone and precipitated into water, and filtered and dried under vacuum at 60°C. The titration data and the IR and ¹H-NMR spectrum of MAPCLA were shown in Table II and Figures 4 and 5, respectively.

The Synthesis of the Carboxyl Telechelic Microspheres

Divinylbenzene was distilled under vacuum before use. BPO (benzoyl peroxide) was recrystallized twice in chloroform.

Cross-linked carboxyl telechelic microspheres were synthesized by suspension polymerization of the MAPCLA with crosslinker divinylbenzene. BPO, gelatin, and toluene were used as initiator, surfactant, and pore-forming agent, respectively.

Table II Esterifications of Oligo-Caprolactone with Maleic Anhydride in Bulk at 80–100°C

Series	Molecular Weight of Oligo-Caprolactone	Maleic Anhydride (Mol % Monomer)	Reactive Efficiency (%)	Molecular Weight		
				By Cal. ^a	By ABT ^b	By NMR
G	245	250	95.2	343	343	330
H	407	250	94.0	505	502	—
I	478	250	97.0	576	584	—
J	508	250	94.0	606	619	—
K	902	250	92.0	1000	1022	—
L	1236	250	92.0	1334	1323	—

^a Cal., calculation.^b ABT, acid-base titration.

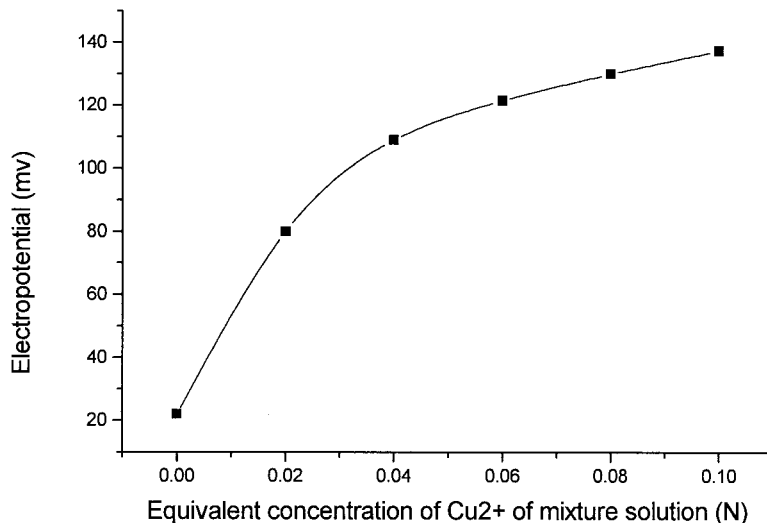


Figure 2 Calibration curve of standard mixture solution of CuCl_2 and NaCl .

Addition of NaCl to the aqueous phase prevented emulsification of the monomer MAPCLA. The size of the beads was controlled by adjusting the volume ratio of the oil to water phase, the stirring speed, and the amount of the surfactant. When the desired droplet size was obtained, the temperature was slowly increased from 40 to 60°C at a rate of 10°C/h, and then further increased to 70°C at a rate of 5°C/h. This program of temperature changes was chosen to ensure that polymerization did not occur too rapidly and to avoid formation of bubbles in the beads. The system was kept at this temperature for about three hours until the beads solidified. The reaction was then allowed to proceed for two successive 10 h periods at 80 and 90°C, respectively.

The product CTMs was washed repeatedly with warm, distilled water for washing off the surfactant (gelatin) and then distilled in water vapor for removal of the pore-forming agent (toluene), dried under vacuum at 60°C for use.

The Measurements of Carboxyl Functionalities of the CTMs

Prior to the studies on the following, the CTMs were swollen in distilled water and treated with approximately 5% HCl solution to fully convert to the hydrogen form resins. To remove excess HCl , the resins were washed repeatedly with distilled water until the neutral elute. Finally, the resins were rinsed with a small amount of methanol and dried under vacuum for use.

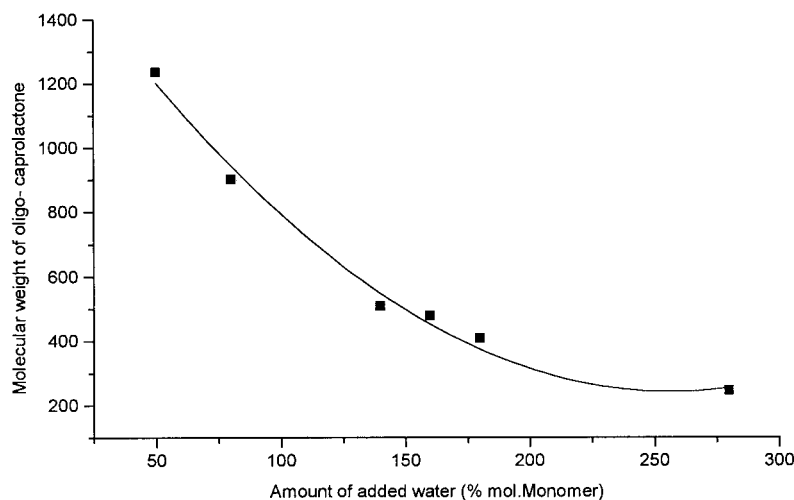


Figure 3 Curve of the molecular weight of oligo-caprolactone for amount of added water.

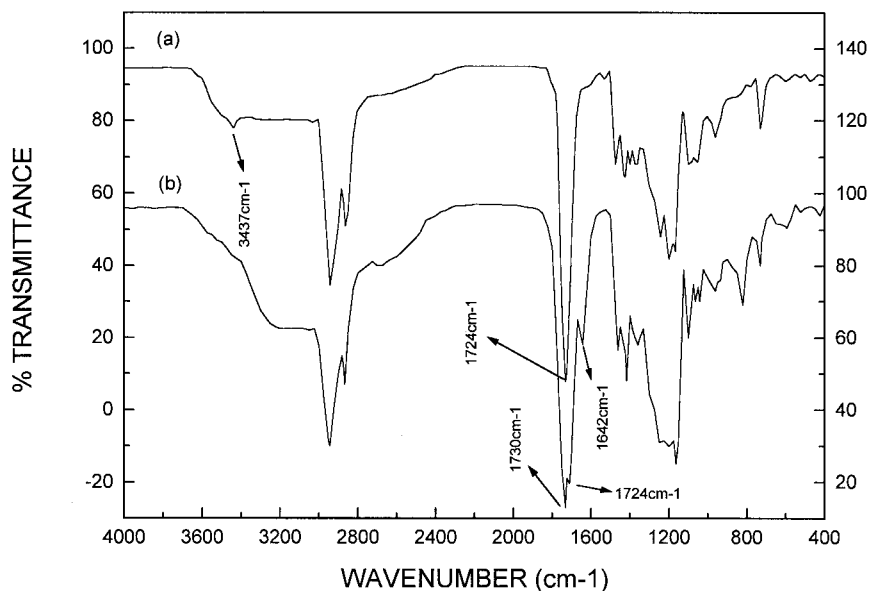


Figure 4 IR spectra of the (a) oligo-caprolactone and (b) MAPCLA in KBr.

The carboxyl functionality of each kind of CTM was determined by acid–base back titration. After the addition of 100.0 mL of 0.1000N NaOH solution to 0.5000N g of dried resin, the sample flask was shaken intermittently for 24

h. 10 mL of solution was sampled for titration. Titrant and indicator was 0.0500N HCl solution and bromcresol green–methyl red, respectively. The computation equation of content of carboxyl was as follows:

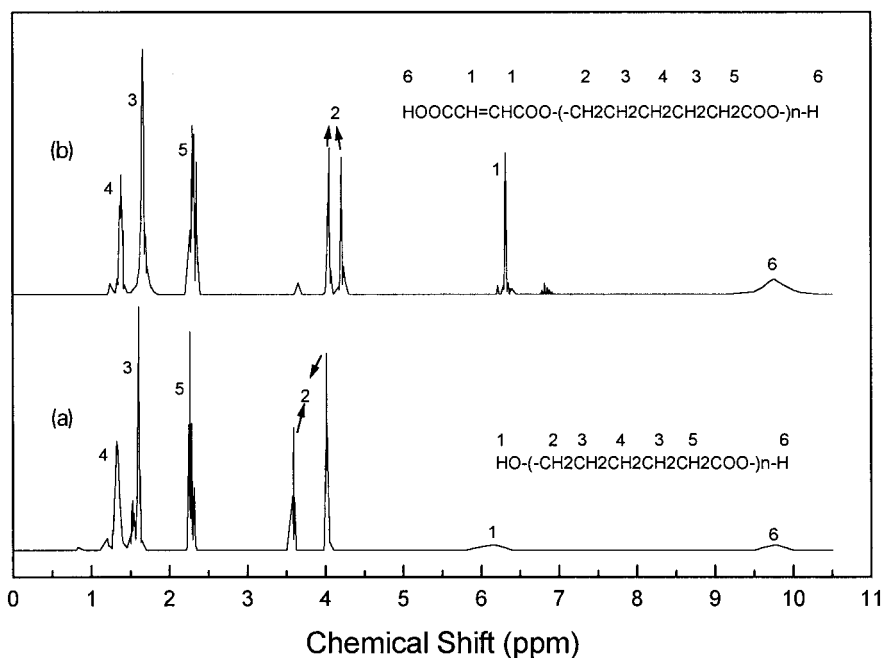


Figure 5 $^1\text{H-NMR}$ spectra: 500 MHz of the (a) oligo-caprolactone and (b) MAPCLA measured in CDCl_3 with internal TMS.

Table III Assignments of $^1\text{H-NMR}$ Spectra of Oligo-Caprolactone and MAPCLA

Assignments		No.	1	2	3	4	5	6	
1	2 3 4 3 5	6	Chem shift	6.1	3.5-4.0	1.5-1.7	1.3	2.4	9.6
HO-($-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{COO}-$) n -H		Integration	1370	4711	9517	4820	4676	1280	
1	2 3 4 3 5	6	Chem shift	6.3	4.0-4.2	1.5-1.8	1.4	2.2-2.4	9.7
HCCOO-($-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{COO}-$) n -H		Integration	344	802	1732	876	843	398	
HCCOOH									
1	6								

Content of carboxyl (mEq/g-CTM)

$$= \frac{(V_1 - V_2) \cdot N \cdot 10}{W}$$

where V_1 is the volume of HCl titrated in blank solution, V_2 is the volume of HCl titrated in sam-

ple solution, N is the equivalent concentration of standard HCl solution, and W is the sample weight of the dried CTMs.

The carboxyl functionalities of the various CTMs and the Emerk.IV resin were measured and are listed in Table IV.

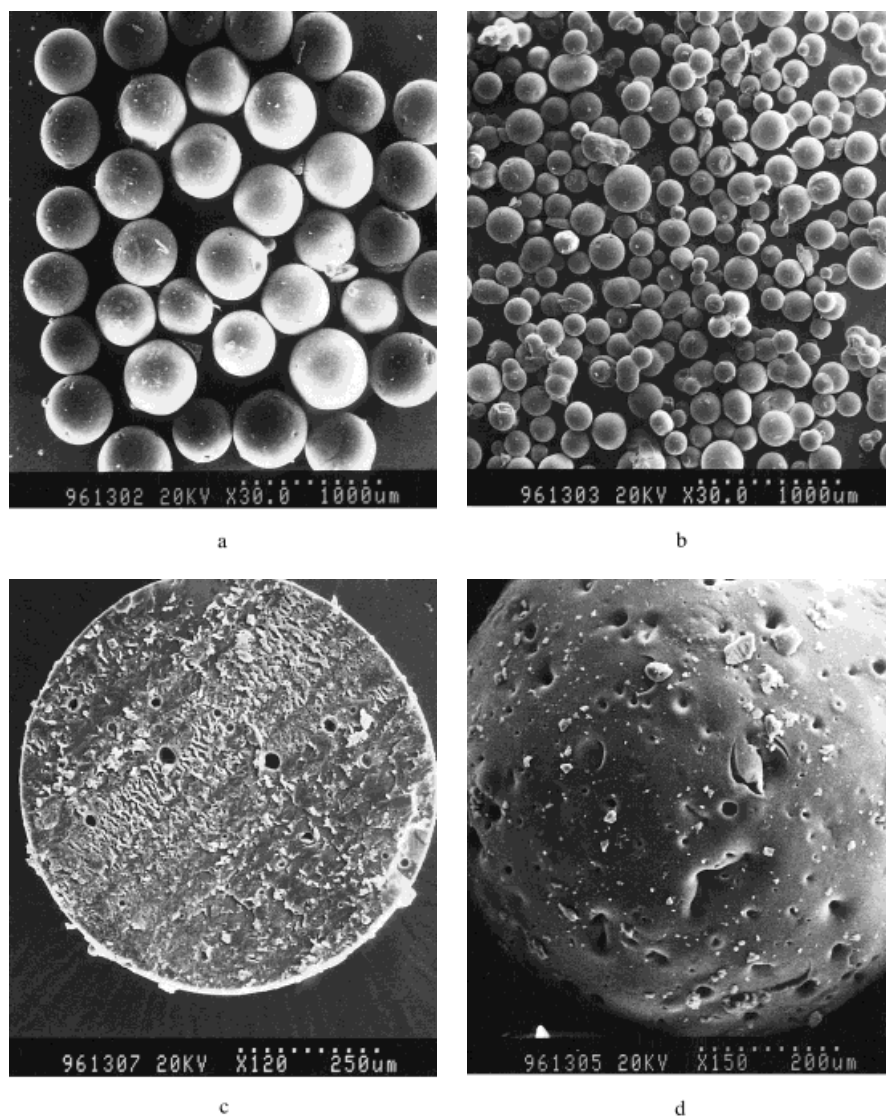
**Figure 6** SEM photographs of the profile and surface of the CTMs.

Table IV Suspension Polymerizations of MAPCLA with Crosslinker Divinylbenzene and Porogen as Toluene and Dichloromethane Initiated with BPO at 60–90°C

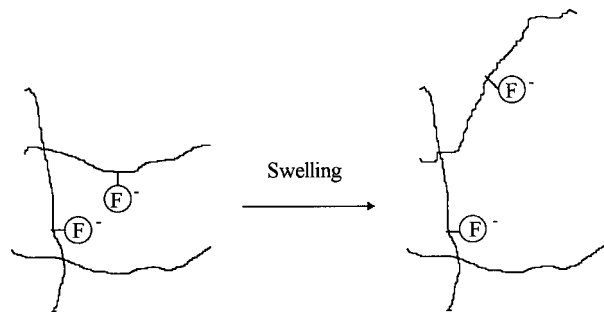
Microspheres	CTM1	CTM2	CTM3	CTM4	CTM5	Emerk.IV
Monomer molecular weight	343	619	619	619	1022	—
Monomer–divinylbenzene (wt)	4/1	4/1	4/1	3/2	3/2	—
Porogen (wt % total monomers)	100	100	50	100	100	—
Crosslinking intensity (%)	20	20	20	40	40	—
Particle size (mm)				0.1–0.5		
Bulk density (g/mL dry resin)	0.49	0.48	0.49	0.53	0.52	—
Content of carboxyl (mEq/g dry resin)	4.2	3.2	3.1	1.7	1.0	10.2
Surface area (m ² /g)						
Adsorption	—	—	—	1.072	0.2988	3.043
Desorption	—	—	—	0.759	0.5216	3.096
Pore volume (mL/g)						
Adsorption	—	—	—	0.0109	0.0041	0.0185
Desorption	—	—	—	0.0059	0.0041	0.0217
Average pore size (Å)						
Adsorption	—	—	—	408.7	559.4	244.0
Desorption	—	—	—	314.8	319.0	280.8

The Measurement of the Water Swellability of the CTM

For practical applications, the degree of swelling in water of the resins is an important property. It is defined by the following equation:

$$\text{Swellability} = \frac{(V_p - V_0)}{V_0} \cdot 100\%$$

where V_0 is the volume of the dry resin and V_p is the volume of the swollen resin. They were measured by adding 0.5 g of the resin to a 10 mL graduated cylinder. After the initial volume of the resin was recorded, the graduated cylinder was filled with distilled water (or 0.5N NaOH solution). The resin was allowed to swell in excess water for more than 24 h, and the final volume was taken. The swellabilities of the CTMs and the Emerk.IV resin are shown in Table V.

**Figure 7** Schematic swelling of the normal resin.

Ion Exchange Procedure

For the exchanging procedure,⁸ the resins need to be converted from hydrogen form to sodium form by dipping them in about 0.1N NaOH solution and washing repeatedly with water. Then the resins were rinsed with a small amount of methanol and dried under vacuum.

0.1N MtCl_2 (where Mt^{2+} represents Cu^{2+} , Co^{2+} , Mg^{2+} , Ba^{2+} , respectively) solution was prepared daily as needed. To measure the rates of $\text{Na}^+ - \text{Mt}^{2+}$ exchange of the resins, a specially designed 60 mL beaker containing 30.00 mL 0.1N MtCl_2 solution equipped with a glass electrode (PHS-3D) and magnetic stirrer was used. After the initial electropotential of the blank solution was recorded, the dry resins (3.0 mEq functionality, 50–70 mesh) were quickly added to the beaker, then gently agitated at room temperature. The electropotential of the mixture solution was recorded every hour until it was constant.

To obtain the exchange amount of the sample

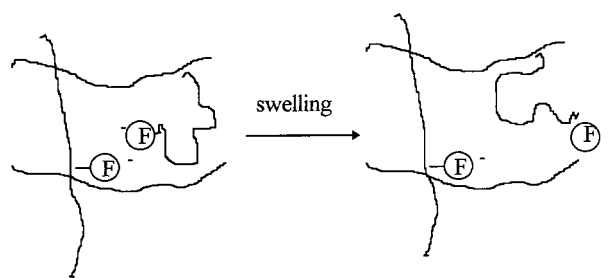
**Figure 8** Schematic swelling of the CTM.

Table V Water Swellabilities of the Resins

Resins	CTM1	CTM2	CTM3	CTM4	CTM5	Emerk.IV
V_0 (mL)	2.0	2.0	2.0	2.0	2.0	2.0
V_{P-H} (mL)	2.3	2.2	2.1	2.1	2.05	3.1
V_{P-Na} (mL)	2.8	2.5	2.3	2.3	2.1	6.5
Swellability (H) (%)	15	10	5	5	2.5	55
Swellability (H-Na) (%)	40	25	15	15	5	225
ΔV (mL)	0.5	0.3	0.2	0.2	0.05	3.4
V (mL)	0.12	0.097	0.066	0.11	0.048	0.31

resin, a calibration curve needs to be plotted. So, six standard solutions, which are 0.1N $MtCl_2$, 0.08N $MtCl_2$, and 0.02N NaCl; 0.06N $MtCl_2$ and 0.04N NaCl; 0.04N $MtCl_2$ and 0.06N NaCl; 0.02N $MtCl_2$ and 0.08N NaCl; and 0.1N NaCl, respectively, were prepared for plotting the calibration curve (as shown in Fig. 2 for $Cu^{2+}-Na^+$).

RESULTS AND DISCUSSION

Effect of the Amount of Water on the Molecular Weight of Oligo-Caprolactone

The hydrolytic oligomerizations of ϵ -Caprolactone were investigated by performing six reaction series in which the amount of added water was varied, as shown in Table I.

In each series, the product ϵ -caprolactone oligomer was characterized by its molecular weight with acid-base titration (ABT), and part of them was checked with hydroxyl value titration (HVT) and 1H -NMR. From the result of series A, the molecular weights calculated by three varies method were coincidental very well. All of the series showed the dependence of the molecular weight of the oligo-caprolactone on the amount of added water. A plot of molecular weight of the oligo-caprolactone versus the amount of added water gave a curve, as shown in Figure 3, which indicated that the molecular weight of oligo-caprolactone decreased as the amount of water increased. The results also indicated that only approximately 16% of the amount of added water acts as an effective initiator. Accordingly, water is a very ineffective initiator. This is coincident with the report of Bassl et al.⁹

The Analysis of the Esterification

The esterifications of oligo-caprolactones with maleic anhydride are shown in Table II. Table II shows that all of the esterifications have a

higher reaction efficiency (>92%). The molecular weights of the product MAPCLA are also determined by ABT and 1H -NMR, as shown in Table II, and coincide with those by calculated from adding the molecular weight of the oligo-caprolactone to that of maleic anhydride.

The Spectroscopic Analysis of the Oligo-Caprolactone and the MAPCLA

To verify the structure of the oligo-caprolactone and the MAPCLA, analysis are performed by IR (NICOLET 170SX FTIR) and 1H -NMR (BRUKER AM-500) spectroscopy, respectively. The IR spectrum of the oligo-caprolactone and the MAPCLA are shown in Figures 4(a) and (b), respectively.

Figure 4(a) is the IR spectrum of the oligo-caprolactone with the biggest peak at 1724 cm^{-1} characteristic of the C=O stretching vibration. The broad peak at $3300\text{--}2400\text{ cm}^{-1}$ is due to end group $-\text{COOH}$ stretching. The small peak at 3437 cm^{-1} is assigned to another end group $-\text{OH}$ stretching vibration. The spectrum of the MAP-

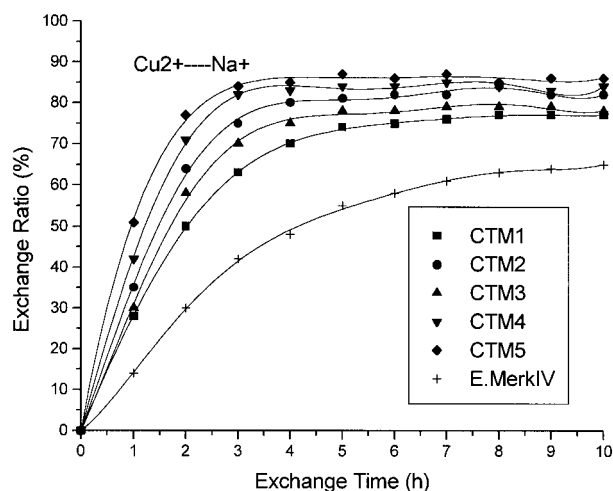


Figure 9 Exchange isotherms, at 15°C, of the CTMs and Emerk.IV.

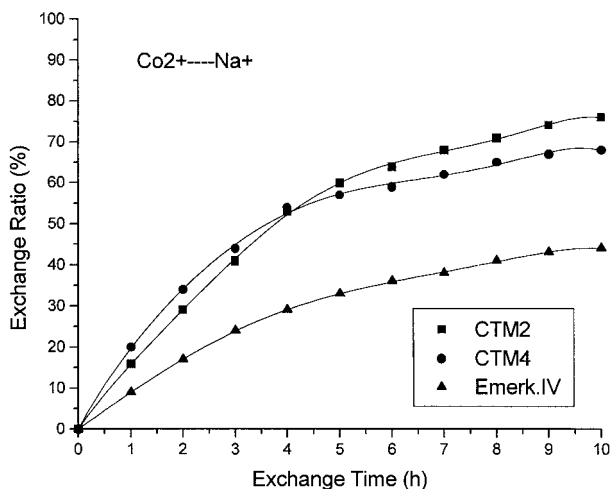


Figure 10 Exchange isotherms, at 15°C, of the selected CTMs with a difference in crosslinking density and Emerk.IV.

CLA is shown in Figure 4(b). The appearance of the C=C stretching peak at 1642 cm^{-1} results from the esterification of the maleic anhydride. The disappearance of the —OH peak at 3437 cm^{-1} in Figure 4(b) also demonstrates that the oligo-caprolactone has been esterified by maleic anhydride. Owing to the esterification, the —COOH peak at $3300\text{--}2400\text{ cm}^{-1}$ in Figure 4(b) is stronger than that in Figure 4(a). The double peaks at 1730 and 1724 cm^{-1} are contributed by the different stretching vibration of carboxyl-carbonyl group and ester-carbonyl group, respectively.

The $^1\text{H-NMR}$ spectra of the oligo-caprolactone and the MAPCLA are shown in Figures 5(a) and 5(b), respectively. Their assignments are listed in Table III.

The Synthesis and Physical Parameter Analysis of the CTMs

MAPCLAs synthesized in this article are a kind of vinyl monomers which are readily polymerized with styrene or divinylbenzene via free radical polymerization. However, due to their high viscosity (waxy or solid state) and poor solubility in toluene, it is difficult for them to be formed microspheres by suspension polymerization. These monomers need to be diluted to a certain concentration of solution before suspension. The CH_3Cl was selected as the solvent mainly because its boiling point is lower than the polymerization temperature. The concentration of monomer in CH_3Cl is a decisive factor in suspension polymer-

ization because the high concentration may affect the appearance of the beads and low concentration will reduce the reactivity of the monomer. At a suitable concentration of monomer (about 50–150%), employing gelatin as the surfactant or stabilizer, the suspension polymerization worked quite well for the preparation of spherical beads (Fig. 6). However, as a result of either inappropriate apparatus design or of insufficient stabilization of the droplet during the sticky phase of polymerization,¹⁰ the problems of coagulation or agglomeration of particles and/or nonspherical particles may be encountered. A series of CTMs with different lengths of telechelic, porous, and crosslinking intensity are synthesized as the procedure described in the experimental section. Their scanning electron microscopy (SEM) photographs are shown in Figure 6. Figures 6(a) and (b) are the SEM photographs of the CTMs with different particle size, respectively. Figure 6(c) is the profile SEM photograph of the CTM. Figure 6(d) is the surface SEM photograph of the CTM. These photographs provide a visual assessment of the appearance, internal structure, and porosity of the CTM.

The carboxyl functionalities and bulk densities of the CTMs are measured and listed in Table IV. Table IV shows that the carboxyl functionality depends on the length of the telechelic chain (monomer molecular weight) and the degree of crosslinking, but independent on the amount of the porogen (toluene).

Some of the prepared CTMs and Emerk.IV resin are also characterized by the pore parameters with BET (Brunauer-Emmett-Teller) (ASAP

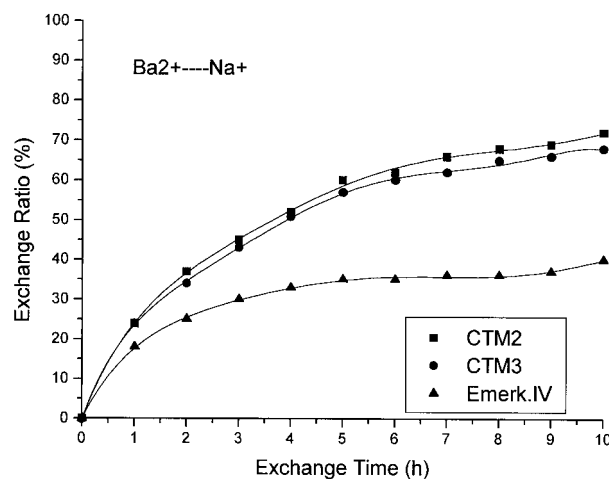


Figure 11 Exchange isotherms, at 15°C, of the selected CTMs with a difference in the amount of porogen and Emerk.IV.

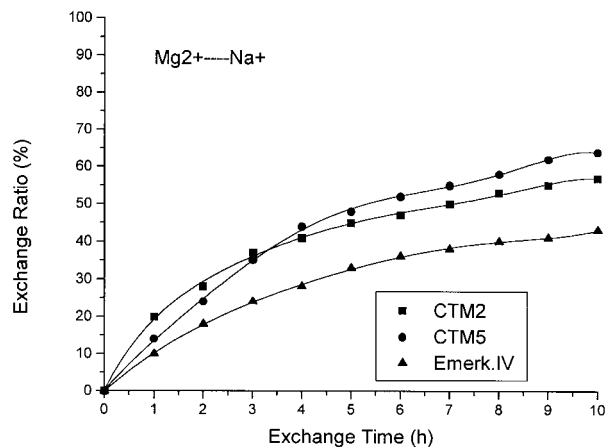


Figure 12 Exchange isotherms, at 15°C, of the selected CTMs with a different length of telechelic chains and Emerk.IV.

2000 V2.02) technology. The results (as listed in Table IV) show whether the surface area or the pore volume of the CTMs are less than those of the Emerk.IV resin, but their average pore size are larger than that of Emerk.IV resin. It seems to be contradictory. Generally, for the polystyrene and polyacrylic acid resin, large pore size will lead to large pore volume. However, as for the CTMs synthesized in this article, the telechelic chains are so flexible that the CTMs may shrink in the BET measuring process. This will make some of the pores (especially small pores) contracted and closed, so the surface area and the pore volume may be less than the actual value.

The Swelling Analysis of the CTMs

For practical application, the nature of the counterion plays a critical role in swelling phenomena. Thus, conversion from one ionic form to another (as in normal exhaustion and regeneration cycles) alters overall resin volume, sometimes significantly. This phenomena may damage the resin and equipment due to the high osmotic pressure developed during swelling. Consequently, it is significant to study the resin with the property of lower volume changing ratio in ion exchange process.

The swelling phenomena of ion exchange resins is the result of both the swelling of the backbone and the repulsion between ionic groups (as shown in Fig. 7).

It is common knowledge that most of the resins have a hydrophobic backbone (as polystyrene) in their matrix. They do not have any swellability in

water unless they are functionalized. Consequently, the repulsion between the ionic group is decisive factor for swelling of the ion-exchange resins.

For normal resins, owing to the short, inflexible pendent groups in their matrix, the repulsion between the groups will have a large effect on the swelling (as shown in Fig. 7). As for the CTMs prepared in this article, because half of the functional groups are linked in the telechelic chains, which may decrease the effect of the repulsion by their free rotation and stretch in wet (as shown in Fig. 8), the swelling will be less than that of the normal resins.

The swellabilities of the five kinds of CTMs are measured by the procedure as described in the experimental section. The Emerk.IV resin is also detected for the comparison. The results in Table V show that all of the swellabilities of the CTMs are less than that of Emerk.IV resin. To discuss the effect of unit carboxyl functionality on the swelling of the resin, the equivalent volume change (V) during conversion from hydrogen form to sodium form is calculated by the total volume change divided with total functionality of the sample resin and listed in Table V. From the V values of the CTM1, CTM2, and CTM5, the effect of the length of the telechelic chains on the swellability of the resin is very remarkable; that is to say, the longer the telechelic chain is, the less the equivalent volume change (V) is. This also indicates that increasing the length of the telechelic chains will decrease the swellabilities of the CTMs.

The Exchange Isotherms of the CTMs

The exchange isotherms, at 15°C, of the selected CTMs and Emerk.IV resin with counterions as

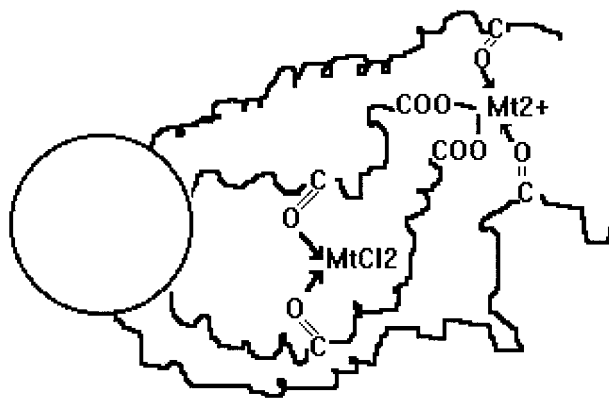


Figure 13 The schematic model of exchange and chelate absorption of divalent ion on the CTMs.

Cu^{2+} , Co^{2+} , Ba^{2+} , and Mg^{2+} , are represented in Figures 9–12, respectively. These exchange isotherms show that, no matter what the counterion is, all of the CTMs possess higher exchange ratio than that of the Emerk.IV resin.

Generally, for the crosslinked resins, the diffusion is the rate-controlling step in the exchange process.¹¹ It is well known that the sizes of the normal hydrated ions are very large, so it is difficult for them to penetrate the highly crosslinked resins. But as for the CTMs synthesized in this article, due to the telechelic chains, which can stretch and rotate in wet conditions, although the hydrated ions have a large size, the penetration in CTMs is still easy. On the other hand, the telechelic chains are not only easy to bind up for exchanging the multivalent ions but also able to follow the chelate absorption (see Fig. 13).

Figure 9 shows the Cu^{2+} – Na^+ exchange isotherms, at 15°C, of the CTMs and Emerk.IV resin for the whole assessment of exchange efficiencies of these resins. Figure 10 is the Co^{2+} – Na^+ exchange isotherms of CTM2 and CTM4 for comparing the effect of the crosslinking density on exchange ratio. From Figure 10, the exchange ratio of the CTM4 is higher than that of the CTM2 in the initial stage, but after 4 h, there is a inverse change in the isotherms. This is because, at the beginning, the exchange sites are mainly located in the surface of the resins; the exchange rate is only decided by the counterion concentration and nearly depends on the inner structure of the resins, so their exchange rates are almost equal. But like the CTM4 with a lower carboxyl functionality, a higher exchange ratio will appear in the isotherm of the CTM4 than in that of the CTM2. As the exchange time goes on, the exchange rate is gradually controlled by the diffusion or penetration step. For CTM4, due to its higher crosslinking density than CTM2, the diffusion may be retarded by the crosslinked networks, and a lower exchange ratio will present in its isotherms.

Figure 11 is the Ba^{2+} – Na^+ exchange isotherms of the CTMs (CTM2, CTM3) with a difference in the amount of porogen. Their exchange ratios are very similar and are much less dependent on the porogen. Figure 12 shows the exchange isotherms of the CTMs (CTM2, CTM5) with different length of telechelic chains. Comparing their isotherms, an increase in the length of telechelic chains (CTM5 > CTM2) increases the exchange ratio, indicating that the exchange ratio is favored by the length of the telechelic chains. But increasing the length of the telechelic chain

will reduce the carboxyl functionality. So the ideal CTMs should have suitable length of the telechelic chains.

CONCLUSIONS

Carboxyl telechelic microspheres (CTMs) with different lengths of oligo-caprolactone telechelic chains have been synthesized by the following reactions: (1) the hydrolytic oligomerization of ϵ -caprolacton, (2) the esterification of oligo-caprolactone with maleic anhydride, and (3) the suspension polymerization of MAPCLA with divinylbenzene. These CTMs, which are water swellable, spherical, and porous, contain carboxyl functionalities of 1.0 to 4.2 mEq/g (dry).

The ring-opening polymerization of ϵ -caprolactone can be initiated by water in the presence of catalyst as dibutyltin dilaurate. The polymerization product is α -hydroxyl, ω -carboxyl oligo-caprolacton; its molecular weight decreases as the amount of water increases. Water acts as a rather ineffective initiator, and its initiation efficiency is only about 16%. The studies on swellability show that all of the CTMs possess low swellabilities in wet. Their equivalent volume changes during conversion from a hydrogen form to a sodium form are also less than that of the Emerk.IV resin.

Systematic studies on the ion exchange by the selected CTMs indicate that (1) all of the CTMs possess higher exchange ratio than that of the Emerk.IV resin; (2) the exchange efficiencies of the CTMs are favored by low crosslinking, but are much less dependent of the porogen; and (3) an increase in the length of the telechelic chains will increase the exchange efficiencies of the CTMs. However, increasing the length of the telechelic chains will also lead to low carboxyl functionalities. Accordingly, the ideal CTMs should contain suitable length of the telechelic chain in their structure.

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