Study of Polyfunctional Carboxyl Telechelic Microspheres

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Received 9 April 1998; accepted 16 September 1998

ABSTRACT: The effects of the hydroxyl group and the carboxyl group on the polymerization of ε-caprolactone (CL) were investigated. The results indicate that the carboxyl group does not initiate the polymerization of CL, but can accelerate the polymerization of CL, which is initiated by the hydroxyl group. Thus, a series of polyfunctional carboxyl telechelic microspheres (PCTMs) with different lengths and number of oligocaprolactone telechelic branch chains, which are capped with two (or three) carboxyl groups at one of these telechelic chains' extremities, were prepared by hydroxy acid (DL-malic acid or citric acid)-initiated polymerization of CL. These PCTMs are water-swellable, spherical, and porous and have both higher total carboxyl amounts and higher telechelic carboxyl ratios than those of the monofunctional carboxyl telechelic microspheres (MCTMs). Their static ion-exchange capacities also increased by increasing the telechelic carboxyl ratios and almost corresponded to the total carboxyl amounts. The intermediate products were characterized by acid–base titration, hydroxyl value titration, ultraviolet, infrared, as well as ^{1}H- and ^{13}C-nuclear magnetic resonance analyses, respectively. The morphology of the PCTMs were characterized by scanning electron microscopy technology. Some of the physical and chemical parameters of the PCTMs are also described. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 667–676, 1999

Key words: ε-caprolactone; hydroxyl acid; telechelic; microsphere

INTRODUCTION

We recently prepared and reported a series of novel monofunctional carboxyl telechelic microspheres (MCTMs) [as shown in Fig. 1(a)].[1] These MCTMs have two different kinds of carboxyl groups, one of which is close to the backbone and the other is a terminal carboxyl group attached to the backbone via a long oligocaprolactone pendent chain. Because these oligocaprolactone telechelic branch chains have certain hydrophilicity and can readily rotate or stretch when wet, the electrostatic repulsion between the ionic groups may decrease. On the other hand, the flexibility of these telechelic branch chains can allow the huge hydrated counterions to pass through the backbone network easily. So, these MCTMs present lower swelling change ratios (during conversion of the ionic form) and higher exchange efficiencies than those of the commercial resin.

However, for these MCTMs, there is only a carboxyl group linked at the end of the telechelic branch chain; thus, their total carboxyl amounts are limited by the length of the telechelic chain. Although a decrease in the length of the telechelic chain may increase the total carboxyl functionality, whereas the telechelic carboxyl ratio in the total carboxyl groups has not changed, decreasing the length of the telechelic chain also decreases the exchange efficiency of the telechelic carboxyl groups. Therefore, how to synthesize a type of carboxyl telechelic microsphere, which has both the high telechelic carboxyl ratios and high total carboxyl amounts, is of important significance.

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Contract grant sponsor: National Natural Science Foundation of China.

Journal of Applied Polymer Science, Vol. 72, 667–676 (1999)
 CCC 0021-8995/99/050667-10

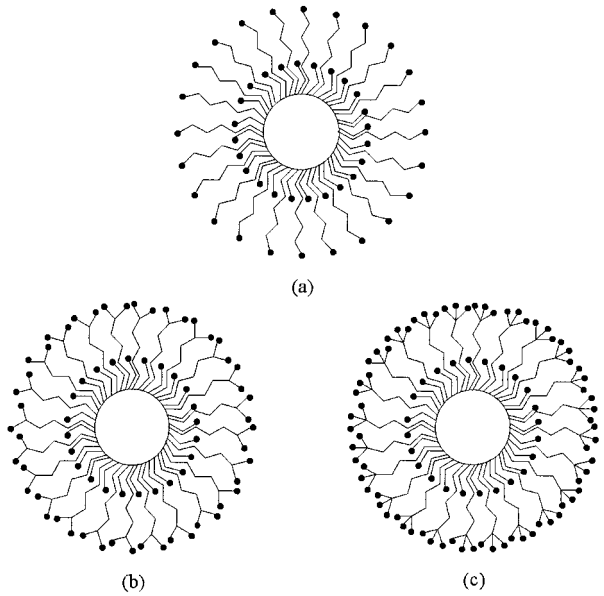
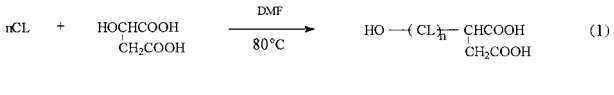
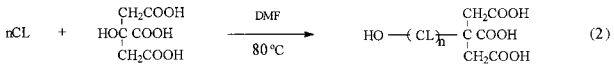


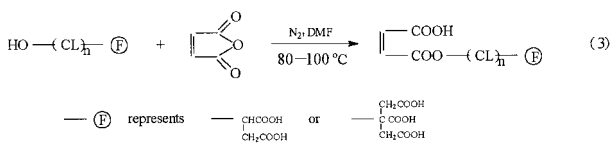
Figure 1 Schematic models of the (a) monofunctional carboxyl telechelic microsphere, (b) bifunctional carboxyl telechelic microsphere, and (c) trifunctional carboxyl telechelic microsphere. (●) Carboxyl group.

In this article, a series of polyfunctional carboxyl telechelic microspheres (PCTMs) [as shown in Figs. 1(b,c)] with different lengths and number of oligocaprolactone telechelic branch chains, which are capped with two (or three) carboxyl groups at one of these telechelic chains' extremities, were designed and synthesized by the following procedures: (1) synthesizing the asymmetric α-hydroxyl and ω-carboxyl[2,3] functional telechelic oligocaprolactones which are initiated by DL-malic acid or citric acid [see eqs. (1) and (2)]:

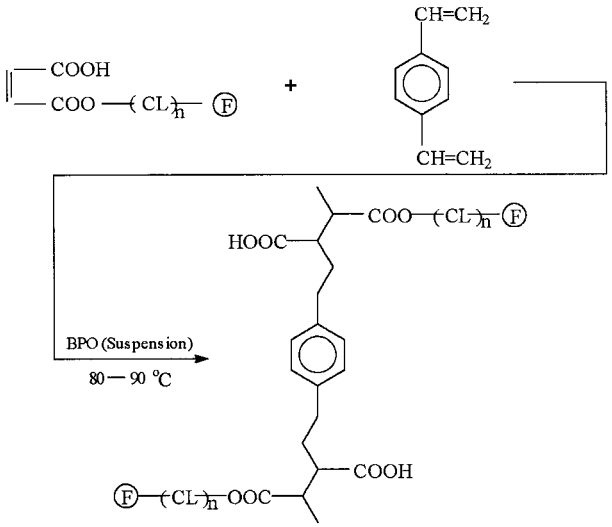




(2) preparing the macromonomers by the esterification of these oligocaprolactones with maleic anhydride [see eq. (3)]:

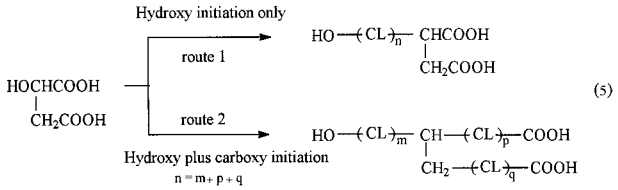


and (3) synthesizing PCTMs by normal suspension polymerization with the crosslinker divinylbenzene [see eq. (4)]:



It is well known that ε-caprolactone (CL) can be generally initiated by the hydroxyl group from alcohol or polyols.[2–6] As of now, studies on the polymerization of CL in the presence of a carboxyl group are very limited. Although some reviewers[2,7] reported that CL can polymerize in the presence of carboxyl acids, however, the polymerization temperature usually decreases to about 200°C, and such a high reaction temperature may cause the polycondensation of hydroxyl groups with carboxyl groups and, thus, complicates the reaction. Estrina et al.[8] studied the kinetics and mechanism of CL anionic polymerization in the presence of aniline and acetic, trifluoroacetic, and hydrochloric acids and suggested that the addition of these proton acids decreased the activation energy of the induction step but without consumption of them, so these proton acids act as catalysts, not as initiators. Bassl et al.[9] thought that the carboxyl acid (acetic acid) did not initiate the polymerization of CL, but acted as a mild retarder in the hydrolytic polymerization of CL by triphenyltin acetate. So, the effect of the carboxyl group on the polymerization of CL is still an open question.

It is well known that DL-malic acid (or citric acid) is a kind of hydroxyl acid containing both hydroxyl and carboxyl groups in the molecular structure. If the hydroxyl group acts as an initiation group only, as in route 1 in eq. (5),



the molecular structure of oligocaprolactone should be a linear chain, and both carboxyl groups are linked at the same end of the telechelic chain. On the contrary, if carboxyl groups also play the initiation role, as in route 2 in eq. (5), the molecular structure may be a branched chain, in which both carboxyl groups will be linked at the different branched chain ends. So, prior to the study of DL-malic acid (or citric acid)-initiated polymerization of CL, the effects of the hydroxyl group and the carboxyl group on the polymerization of CL should be clarified.

This article was concerned mainly with the effects of the hydroxyl group and the carboxyl group on the polymerization of CL. The oligomerizations of CL initiated by hydroxyl acids (DL-malic acid and citric acid) were investigated. The synthesis and characterization of PCTMs are also described.

EXPERIMENTAL

Materials

The monomer CL (Aldrich) was dried over calcium hydride at room temperature for 24 h, then distilled under reduced pressure (bp 110°C/12 mmHg) before use. DL-Malic acid, citric acid, and *n*-butyric acid were milled and sieved to 100 mesh, then dried in a vacuum oven (60°C) for at least 24 h. *n*-Butyl alcohol and trifluoroacetic acid were distilled before use. Benzoic acid was purified by sublimation.

Measurements

Infrared (IR) spectra were obtained on a Nicolet 170SX FTIR spectrometer in KBr. Ultraviolet (UV) spectra were tested on an HP8453 UV-visible spectrometer. A 0.05% ethanol solution was measured in a quartz pool.

The 500-MHz ^{1}H-nuclear magnetic resonance (^{1}H-NMR) spectrum was recorded on a Bruker AM-500 spectrometer. A solution of a 50-mg sample in 0.5 mL of a deuterated dimethyl sulfoxide (DMSO-d_6) solvent was measured in a 5-mm-o.d. sample tube. The 500-MHz ^{13}C-nuclear magnetic resonance (^{13}C-NMR) spectrum was obtained on a Bruker AM-500 spectrometer in a 5-mm-o.d. sample tube containing 200 mg of oligocaprolactone in 0.5 mL of DMSO-d_6.

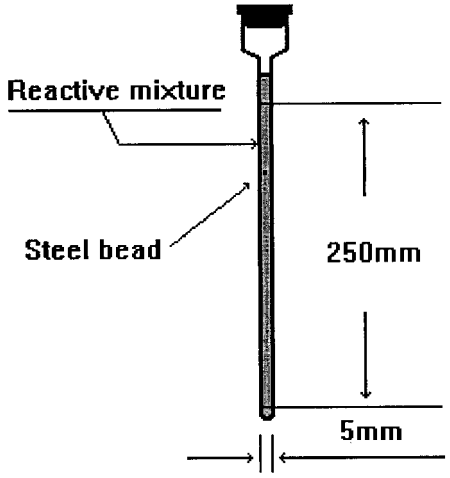


Figure 2 Polymerization tube for measuring the bulk viscosity of the polymerization mixture.

The measurement of the hydroxyl value of oligocaprolactone was proceeded by a normal hydroxyl value titration (HVT) in which the sample was first treated with maleic anhydride in *N,N*-dimethylformamide (DMF) under nitrogen at 80–100°C so that the new carboxyl group in a number equivalent to the original hydroxyl group was liberated, then subjected to acid–base titration (ABT) for determining the total content of the carboxyl group.

The content of the carboxyl group of the sample was measured by normal ABT. The titrant and indicator were a 0.05*N* NaOH alcohol solution and phenolphthalein, respectively.

Measurement of Bulk Viscosity of the Polymerization Mixture

The bulk viscosity of the polymerization mixture was measured in a specially designed polymerization tube (as shown in Fig. 2). After the polymerization mixture was added to the tube, a process of two successive vacuums and purgings of nitrogen was needed for degassing at room temperature. Then, the polymerization tube was placed in an 80°C water bath. A steel bead was adjusted at a certain height by a magnet and the descending time (i.e., bulk viscosity) of the steel bead in the reaction mixture was measured with a high-precision stopwatch (0.01 s) every 6 h until the desired reaction time.

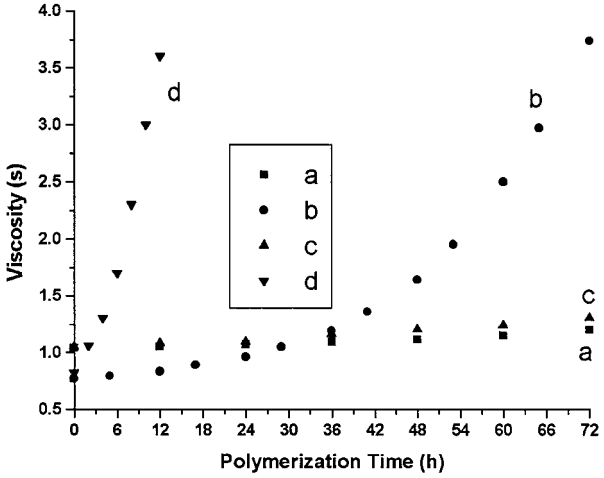


Figure 3 Polymerization viscosity curves of CL with various additives: (a) *n*-butyric acid only; (b) *n*-butyl alcohol only; (c) *n*-butyric acid plus trifluoroacetic acid; (d) *n*-butyl alcohol plus trifluoroacetic acid.

Polymerization Investigation of CL in the Presence of Benzoic Acid

The reaction proceeded in a 100-mL flask. The mixture of 0.01mol CLand 0.01 mol benzoic acid was added to the flask. After reaction under nitrogen at 80°C for 72 h, a small amount of the reactive mixture was sampled to be sublimed under a vacuum (10 mmHg) at 120°C for 24 h, then subjected to the IR and UV analyses, as shown in Figures 3 and 4, respectively.

Oligomerization of Caprolactone Initiated by DL-Malic Acid and Citric Acid

All of the polymerizations were performed in a 250-mL Wolff bottle equipped with a ball condenser, an isobaric funnel, and a magnetic stirrer and protected under nitrogen. After the stoichiometric amount of the initiator was weighed into the bottle, a proper amount of anhydrous DMF solvent was added. After the initiator was completely dissolved in DMF, the temperature of the silicone oil bath increased to 80°C; then, the monomer CL was slowly dropped from the isobaric funnel into the bottle at the speed of 3 d/min. When the dropping was finished, the polymerization was kept at 80°C for 6–8 h. At the end of the reaction, the product mixture was precipitated twice from DMF into water to remove the unreacted monomer and initiator; then, the sample was filtered and dried under a vacuum at 60°C for 24 h.

Esterification of the Oligocaprolactones with Maleic Anhydride

The esterification [as in eq. (2)] proceeded in the DMF solvent under nitrogen protection in a flask with a ball condenser and a magnetic stirrer. The oligocaprolactone 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 precipitated twice from DMF into hot water (90°C) to remove the unreacted maleic anhydride; then, the sample was filtered and dried under vacuum at 60°C for 24 h.

Preparation and Measurement of Carboxyl Amount of the PCTMs

The preparation and the measurement methods of the carboxyl amount of the PCTMs are similar to those of the MCTMs, as described in a previous article.[1]

Measurements of the Static Ion-exchange Capacity and Efficiency of the PCTMs

For the measurements of the static ion-exchange capacity and efficiency of the PCTMs, the PCTMs needed to be converted from the hydrogen form to the sodium form by dipping them in about a 0.1*N* NaOH solution and washing repeatedly with water. Then, the resins were rinsed with a small amount of methanol and dried under a vacuum at 60°C.

A 0.1*N* $MtCl_2$ (where Mt^{2+} represents Cu^{2+} or Co^{2+}) solution was prepared daily as needed. To measure the rates of Na^+—Mt^{2+} exchange of the

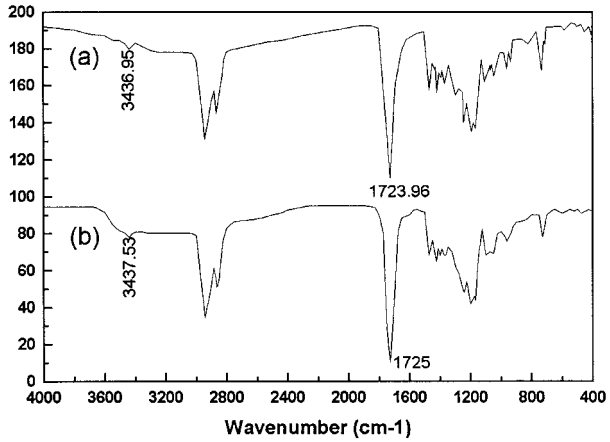


Figure 4 IR spectra of (a) the reaction mixture sample after being sublimed and (b) the oligocaprolactone synthesized by water-initiated polymerization of CL.[1]

Table I Polymerization Runs of CL in Bulk with Various Additives at 80°C

Series	Monomer	Additives (% mol of Monomer)	Polymerization Condition
a	CL 5.0g	*n*-Butyric acid (10)	Bulk, 80°C,
b		*n*-Butyl alcohol (10)	under nitrogen
c		*n*-Butyric acid (10) + trifluoroacetic acid (1 μL)	
d		*n*-Butyl alcohol (10) + trifluoroacetic acid (1 μL)	
e		Benzoic acid (100)	

resins, a specially designed 60-mL beaker containing a 30.00 mL 0.1*N* $MtCl_2$ 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. After 24 h, the electropotential of the mixture solution was recorded; then, according to the calibration curve (as described in ref. 1), the static ion-exchange capacity and efficiency of the PCTMs could be calculated.

RESULTS AND DISCUSSION

Effect of Hydroxyl and Carboxyl Groups on the Polymerization of CL

To qualitatively analyze the effect of the hydroxyl and carboxyl groups on the polymerization of CL, four reaction series, as shown in Table I, were performed in a specially designed polymerization tube (as shown in Fig. 2) in order to easily trace the reaction level by measuring the bulk viscosity of the polymerization mixture. Figure 3 shows the polymerization viscosity curves of runs a–d. As can be seen from curve a, in which the additive is *n*-butyric acid, the viscosity shows nearly no change as the polymerization time continues. However, curve b, which represents *n*-butyl alcohol as the additive, the viscosity increases versus the reaction time. This qualitatively indicates that the hydroxyl group but not the carboxyl group can effectively initiate the polymerization of CL at moderate temperature. On the other hand, if a small amount of trifluoroacetic acid was added to run b, the polymerization rate will increase sharply (compare curve d with curve b), whereas the addition of trifluoroacetic acid to run a did not affect the polymerization rate at all (see curves a and c). So, the carboxyl group can hardly initiate the polymerization of CL, but an amount of the strong carboxyl acid can accelerate the hydroxyl group to initiate the polymerization of CL.

For further verifying the above-mentioned conclusion, a test was designed by enlarging the amount of the carboxyl acid additive, as shown in Table I (run e). Benzoic acid was selected as the additive mainly because its benzene ring can be easily tested by IR and UV technologies. The polymerization was as described in the Experimental part. The IR and UV analyses are shown in Figures 4 and 5, respectively.

Figure 4(a) shows the IR spectrum of the reaction mixture after being sublimed. If benzoic acid could initiate the polymerization of CL, the oligocaprolactone (i.e., reaction product) should contain the composition of the benzene ring. But from Figure 4(a), there is no sign of the benzene ring

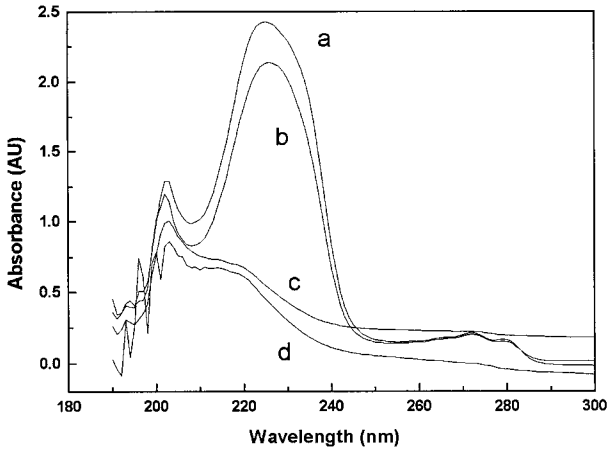


Figure 5 UV spectra of (a) benzoic acid, (b) the reaction mixture, (c) the reaction mixture sample after being sublimed, and (d) oligocaprolactone synthesized by water-initiated polymerization of CL[1] and a 0.05% solution of anhydrous ethanol.

Table II Oligomerizations of CL Initiated by Different Kinds and Amounts of Hydroxyl Acids in DMF Under Nitrogen at 80°C

Runs	Initiator	Mole Ratio of Initiator to Monomer	Addition Method of Monomer	Molecular Weight of Oligo-caprolactone	Initiation Efficiency (%)	Content of Carboxyl Group (10^{-3} g/mol)	Content of Hydroxyl Group (10^{-3} g/mol)	Mole Ratio of OH to —COOH
f	MA	1 : 3	Total	820	49.9	2.44	—	—
g	MA	1 : 3	Drop	502	93.1	3.98	1.95	1/2.04
h	CA	1 : 5	Drop	781	88.2	2.56	1.24	1/2.07
i	CA	1 : 3	Drop	612	81.5	4.90	1.60	1/3.06
j	CA	1 : 5	Drop	880	83.0	3.41	1.10	1/3.10

MA, DL-malic acid; CA, citric acid.

vibration peak (which should be at 1500, 1580, and 1600 cm^{-1}), and Figure 4(a) is very similar to Figure 4(b), which represents the IR spectrum of oligocaprolactone synthesized by water-initiated polymerization of CL.[1] Also, from the UV spectrum [Fig. 5(c)], the E_1, E_2, and B absorbency of the benzene ring cannot be observed. All these results demonstrate that the benzoic acid did not initiate the polymerization of CL.

Effect of DL-Malic Acid and Citric Acid on the Polymerization of CL

DL-Malic acid and citric acid are a series of hydroxyl acids containing both hydroxyl and carboxyl groups in the molecular structure. According to the carboxyl-catalyzed hydroxyl group-initiated polymerization of CL, these hydroxyl acids can initiate the polymerization of CL by the hydroxyl group, whereas the carboxyl groups do not play the initiation role, but can accelerate the hydroxyl-initiated polymerization of CL. On the other hand, to avoid the esterification of the hydroxyl group with the carboxyl group at high temperature, the polymerization has to be controlled at a moderate temperature. In this article, all the polymerizations were performed at about 80°C.

Table II lists the polymerizations of CL initiated by different kinds and amounts of hydroxyl acids (DL-malic acid, citric acid) in DMF under nitrogen at 80°C. For the DL-malic acid- or citric acid-initiated polymerization of CL, Table II shows the dependence of the molecular weight of oligocaprolactone on the amount of the added hydroxyl acid initiator (see runs g–j). In addition, as a result of the different reactivities between the initiation and propagation steps, the molecular weight of oligocaprolactone is also affected by the addition method of the monomer (comparing run f with run g).

On the other hand, for these hydroxyl acid-initiated polymerizations of CL, esterification between the hydroxyl group and the carboxyl group must be investigated, because esterification will affect the molecular structure of oligocaprolactone. Usually, an intramolecular esterification causes the formation of cyclic oligomers and intermolecular esterification modifies the chain structure of oligocaprolactones. Both intra- and intermolecular esterification will cause an ill-defined molecular structure of oligocaprolactone. In this article, the esterification level was also evaluated by comparing the mole ratio of the hydroxyl group to the carboxyl group of the oligocaprolactone with that of the hydroxyl acid (DL-malic acid or citric acid). It is clear that the hydroxyl group and carboxyl group are consumed as an equivalent mole number in the esterification. Thus, for the oligocaprolactone which was produced by DL-malic acid- or citric acid-initiated polymerization of CL, while in the absence of esterification, the mole ratio of hydroxyl to carboxyl groups should be equal to that of the hydroxyl acid, that is, 1/2 for DL-malic acid and 1/3 for citric acid, whereas in the presence of esterification, this mole ratio should be less than that of the hydroxyl acid.

Table II shows the results from the ABT and HVT measurements. From Table II, for the different hydroxyl acid initiators, the oligocaprolactones have almost equivalent mole ratios of hydroxyl to carboxyl groups to that of the corresponding hydroxyl acid. So, at a moderate reaction temperature, the esterification reaction can be neglected for these hydroxyl acid-initiated polymerizations of CL. Table II also shows that an approximately 80–90% amount of hydroxyl

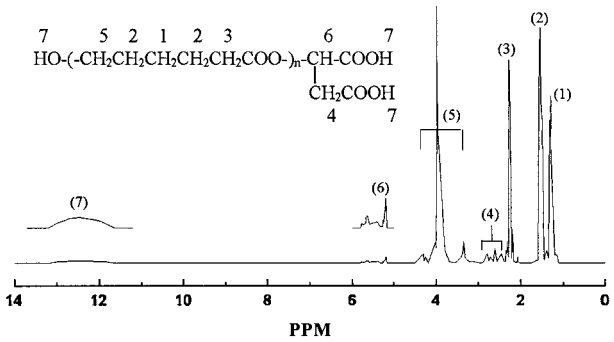


Figure 6 500-MHz ^{1}H-NMR spectrum of oligocaprolactone initiated by DL-malic acid measured in DMSO with internal TMS.

acid acts as an effective initiator; this is much more than that of the water-initiated (only 16%) polymerization of CL.[1]

Spectroscopic Analysis of the Oligocaprolactones and Related Esterified Products and the PCTMs

To verify the structures of oligocaprolactones and the relevant products, analyses were performed by both IR and NMR spectroscopy. Figure 6 shows the ^{1}H-NMR spectrum of oligocaprolactone which was produced by DL-malic acid-initiated oligomerization of CL. The number seven peak at 12.45 is due to the quick exchange of the protons between the hydroxyl and carboxyl groups, whereas the single hydroxyl and carboxyl proton-absorbed peaks cannot be seen. From the number four peak, if the adjacent carboxyl group participates in the initiation polymerization of CL, and as a result of the identical adjacent ester group, the number four peak should coincide with the number three peak. On the other hand, due to the hydrogen bond effect of the adjacent carboxyl groups, the number six and number four hydrogen atoms present split the absorbed peaks. Figure 7 shows the ^{13}C-NMR spectrum of the oligocaprolactone initiated by DL-malic acid. The detailed assignments of various carbon atoms are shown in Figure 7. The different absorbency between the number five and number four carbon atoms also demonstrates that the adjacent group of the number five carbon atom is the carboxyl group, not the ester group.

Figure 8(a) shows the IR spectrum of the oligocaprolactone initiated by DL-malic acid. The biggest peak at 1732.4 cm^{-1} belongs to the characteristic $\nu_{C=O}$. The small peak at 3443.1 cm^{-1} is assigned to the end hydroxyl group stretching vibration. The broad peak at 3300–2400 cm^{-1} is due to the ν_{O-H} of the end carboxyl groups. The peaks at 1235.5 and 1166.7 cm^{-1} are attributed to the ν_{CO-O-C} stretching vibration.

Figure 8(b) shows the IR spectrum of the esterified oligocaprolactone product by maleic anhydride. The appearance of the $\nu_{C=C}$ stretching vibration peak at 1645.5 cm^{-1} demonstrates that the oligocaprolactone has been esterified by maleic anhydride.

Figure 8(c) shows the IR spectrum of telechelic microspheres. The peaks at 1603.9 and 1510.7 cm^{-1} as well as peaks at 797.3 and 708.7 cm^{-1} clearly show the existence of the benzene ring. In addition, the disappearance of the $\nu_{C=C}$ peak at 1645.5 cm^{-1} in Figure 3(b) also indicates that the

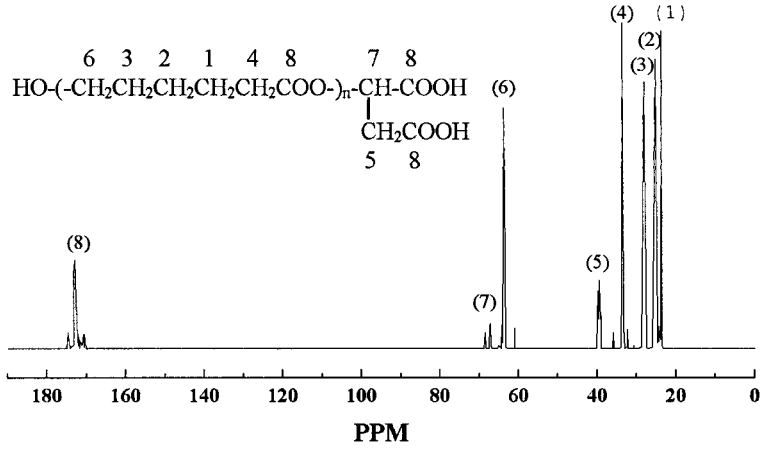


Figure 7 500-MHz ^{13}C-NMR spectrum of oligocaprolactone initiated by DL-malic acid measured in DMSO with internal TMS.

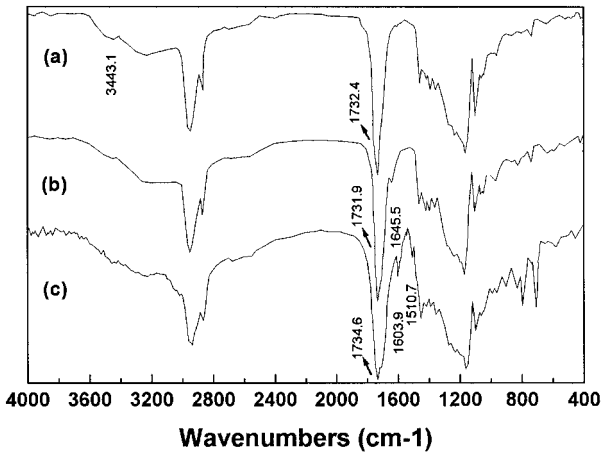


Figure 8 IR spectra of (a) oligocaprolactone initated by DL-malic acid and (b) the esterified product as well as (c) the bifunctional carboxyl telechelic microspheres.

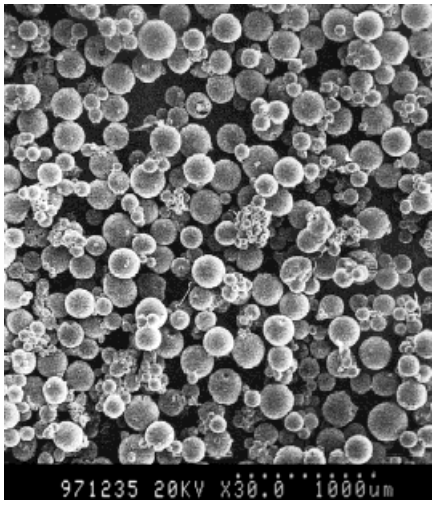


Figure 10 SEM photograph of the PCTMs.

esterified oligocaprolactone product has completely reacted with the divinylbenzene.

Figure 9 also shows a series of IR spectra which relate to the citric acid-initiated oligocaprolactone. All the assignments are similar to those in Figure 8.

Synthesis and Parameters Analysis of the PCTMs

The esterified oligocaprolactones are a kind of vinyl monomers which are readily polymerized with divinylbenzene via a free-radical polymerization. However, these monomers are usually present in a solid state at room temperature. So, prior to the suspension polymerization, these monomers need to be diluted to a certain concentration of the solution. DMF was selected as the solvent mainly because these monomers have good solubility in it. On the other hand, for preventing the emulsification of the suspension mixture, a saturated NaCl water solution was used as the suspension aqueous phase. The concentration of a monomer in DMF is a decisive factor in suspension polymerization, because high concentration may increase the viscosity of the suspension mixture and affect the appearance of the beads and low concentration will both reduce the reactivity of the monomer and lead to the agglomeration of the particles. Thus, at a suitable concentration of the monomer, employing gelatin as the surfactant or stabilizer, the suspension polymerization worked quite well for the preparation of spherical beads. SEM photographs of the PCTM are shown in Figure 10. However, as a result of either an inappropriate apparatus design or an insufficient stabilization of the droplet during the sticky phase of polymerization, the problems of the coagulation or agglomeration of particles and/or nonspherical particles may be encountered.

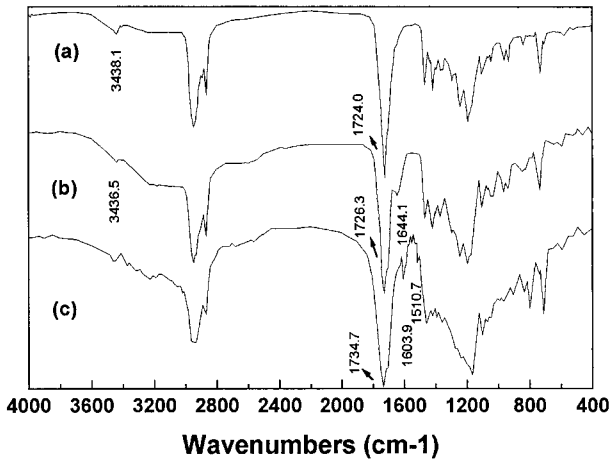


Figure 9 IR spectra of the (a) oligocaprolactone initated by citric acid and (b) the esterified product as well as (c) the trifunctional carboxyl telechelic microspheres.

The carboxyl amounts of various PCTMs were measured and are listed in Table III. Table III shows that the carboxyl amounts of these PCTMs depend both on the initiators and on the length of the telechelic branch chain (monomer molecular weight). Comparing MCTM4, PCTM1, and PCTM3, three kinds of microspheres have a similar monomer molecular weight, but due to the different initiators, their carboxyl amounts are

Table III Physical Parameter Comparison of Various Carboxylic Telechelic Microspheres

	Telechelic Microspheres					
	MCTM4	MCTM5	PCTM1	PCTM2	PCTM3	PCTM4
	Initiators					
Physical Parameters	Water	Water	MA	MA	CA	CA
No. telechelic carboxyl groups	1	1	2	2	3	3
Monomer molecular weight	619	1022	595.2	860.7	722.4	992.0
Monomer—divinylbenzene (wt)	3/2	3/2	3/2	3/2	3/2	3/2
Amount of carboxyl groups (meq/g)	1.7	1.0	2.9	2.0	3.3	2.3
Static ion-exchange capacity (meq/g)						
Cu^{2+}	1.528	0.943	2.639	1.910	3.046	2.346
Co^{2+}	1.498	0.901	2.540	1.788	2.993	2.220
Static ion-exchange efficiency (%)						
Cu^{2+}	89.9	94.3	91.0	95.5	92.3	98.0
Co^{2+}	88.1	90.0	87.6	89.4	90.7	96.5

MCTM4 and MCTM5 were synthesized in a previous article.[1] MA, DL-malic acid; CA, citric acid.

varied, and the carboxyl functionality ratio of PCTM1 to MCTM4 (2.9/1.7 ≅ 1.7) is close to the theoretical value, that is, (2 + 1)/(1 + 1) = 1.5. Similarly, for MCTM5, PCTM3, and PCTM4, the dependence of the carboxyl amounts on the initiators also can be observed, and the carboxyl functionality ratio of PCTM4 to MCTM5 (2.3/1.0 = 2.3) is similar to the theoretical value of (3 + 1)/(1 + 1) = 2. So, the carboxyl amounts of the telechelic microspheres can increase either by decreasing the length of the telechelic branch chain or using the polycarboxyl hydroxyl acid initiators.

The static ion (Cu^{2+} and Co^{2+})-exchange capacities of these telechelic microspheres were also measured and are shown in Table III. The static ion-exchange capacities of these telechelic microspheres almost correspond to their total carboxyl amounts. Also, all of them present higher exchange efficiencies (>90%).

The dynamic ion-exchange isotherms, at 15°C, of the selected microspheres (MCTM4, PCTM1, PCTM3) which differ in the number of telechelic carboxyl groups and are similar in the length of telechelic chains are given in Figures 11 and 12. From these exchange isotherms, whether the exchange counterion is Cu^{2+} or Co^{2+}, three kinds of telechelic microspheres possess the higher exchange ratios than that of the E. Merck IV resin. As for the dynamic exchange ratio, three kinds of telechelic microspheres are very similar from 0 to 4 h. Only after 4 h, a slight increase which may be affected by the number of telechelic carboxyl groups can be seen from their exchange isotherms as PCTM3 > PCTM1 > MCTM4.

CONCLUSIONS

The ring-opening polymerization of CL can be initiated by DL-malic acid and citric acid with a self-catalyzed reaction at moderate temperature (80°C). These hydroxyl acids can initiate the poly-

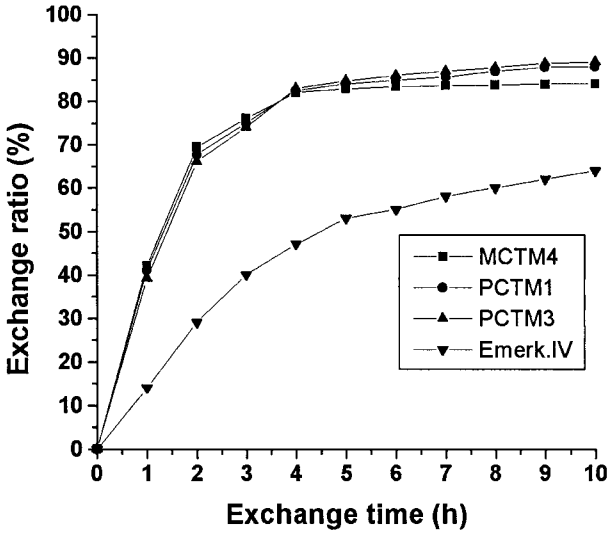


Figure 11 Exchange isotherms, at 15°C, of the selected telechelic microspheres and the E. Merck IV resin with the counterion as Cu^{2+}.

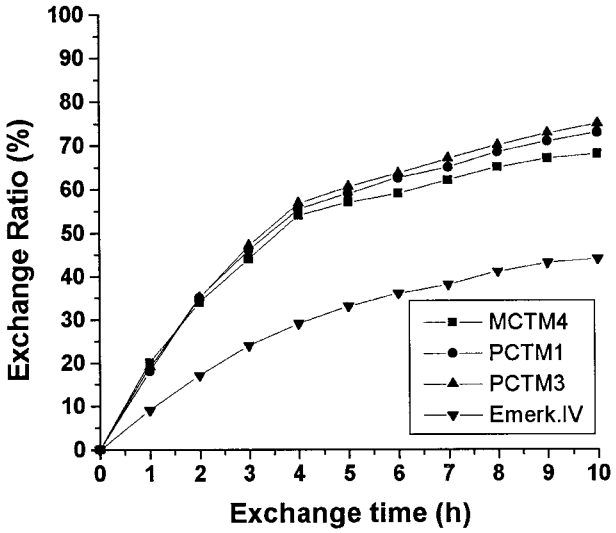


Figure 12 Exchange isotherms, at 15°C, of the slected telechelic microspheres and the E. Merck IV resin with the counterion as Co^{2+}.

merization of CL by the hydroxyl groups, whereas the carboxyl groups do not play the initiation role but can accelerate the polymerization. Thus, a series of asymmetric α-hydroxyl and ω-carboxyl[2,3] functional telechelic oligocaprolactones can be readily obtained. The molecular weight of these oligocaprolactones is affected by both the amount of the added initiator and the addition method of the monomer. The initiation efficiencies (80–90%) of DL-malic acid and citric acid are much more than that of water (only 16%).

PCTMs with different lengths and number of oligocaprolactone telechelic branch chains, which are capped with two (or three) carboxyl groups at one of these telechelic chains' extremities, can be prepared by the following procedures: (1) synthesizing the asymmetric α-hydroxyl and ω-carboxyl[2,3] functional telechelic oligocaprolactones by DL-malic acid- (or citric acid)-initiated oligomerization of CL, (2) preparing the macromonomers by the esterification of these oligocaprolactones with maleic anhydride, and (3) synthesizing the PCTMs by normal suspension polymerization with the crosslinker divinylbenzene.

The carboxyl amounts of these carboxyl telechelic microspheres can be increased either by decreasing the length of the telechelic branch chain or using the polycarboxyl hydroxyl acid initiators (such as DL-malic acid and citric acid). These PCTMs have both higher total carboxyl amounts and higher telechelic carboxyl ratios than those of the MCTMs. Their static ion-exchange capacities also increase with increasing the telechelic carboxyl ratios and almost correspond to the total carboxyl amounts. The dynamic ion-exchange ratios of these PCTMs only show a slight increase.

This research was supported in part by the National Natural Science Foundation of China.

REFERENCES

1. Xie, D.-L.; Ge, H.-X.; Zhang, L.-X.; Yang, C.-Z. J Appl Polym Sci 1998, 68, 205–216.
2. Brode, G. L.; Koleske, J. V. J Macromol Sci-Chem A 1972, 6, 1109–1144.
3. Leenslag, J. W.; Pennings, A. J. Makromol Chem 1987, 188, 1809.
4. Kricheldorf, H. R.; Berl, M.; Sharnagl, N. Macromolecules 1988, 21, 286.
5. Cherdron, H.; Ohse, H.; Korte, F. Makromol Chem 1962, 56,179.
6. Saotome, K.; Kodaira, Y. Makromol Chem 1965, 82, 41.
7. Lofgren, A.; Albertsson, A. C.; Dubois, P.; Jerome, R. JMS-Rev Macromol Chem Phys 1995, 35, 379–418.
8. Estrina, G. A.; Davtyan, S. P.; Rozenberg, B. A. Vysokomol Soedin Ser A 1979, 21, 2235–2240 (in Russian).
9. Bassl, M. B.; Padlas, A. B.; Hall, H. K., Jr. Polym Bull 1990, 24, 227–232.