1574 *Macromolecules* **2009**, *42*, 1574−1579

Polycaprolactone-Based Novel Degradable Ionomers by Radical Ring-Opening Polymerization of 2-Methylene-1,3-dioxepane

Agarwal Seema* and Ren Liqun

Philipps-Universität Marburg, Fachbereich Chemie, Hans Meerwein Strasse,
D-35032 Marburg, Germany

Received November 21, 2008; Revised Manuscript Received January 5, 2009

ABSTRACT: This work reports the first successful synthesis of polycaprolactone (PCL)-based degradable ionomers using free-radical chemistry. Degradable cationic ionomers were synthesized by random radical terpolymerization of 2-methylene-1,3-dioxepane (MDO), methyl methacrylate (MMA), and *N,N*-dimethylaminoethyl methacrylate (DMAEMA) and followed by quaternization of amine with alkyl bromide. The terpolymerization of MDO, MMA, and DMAEMA led to a polymer with ester group randomly distributed in the polymer chains. The small-angle X-ray scattering (SAXS) analysis, the transmission electron microscope (TEM), and dynamic mechanical analysis (DMA) showed ionic aggregates existing in ionomers. Ionomers quaternized by ethyl bromide showed relative strong ionic interaction and showed aggregates with a diameter around 30 nm, which had a separate glass transition temperature (T_g) and performed rather as filler material. Ionomers containing 40 mol % of ester group and 20 mol % of ionic group showed biodegradability after being buried in compost.

Introduction

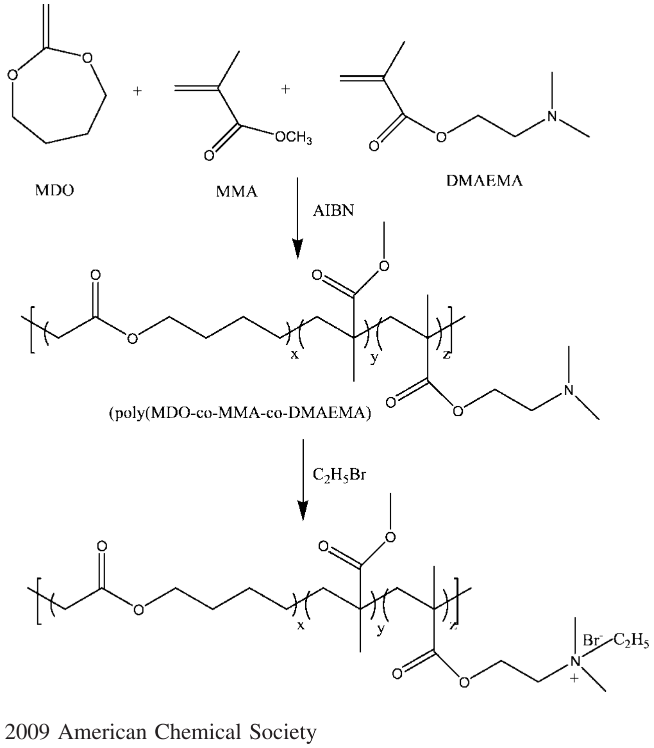
There has been considerable interest in the synthesis of aliphatic polyesters due to the growing importance of environmentally degradable polymers and for various biomedical applications. Mainly, copolymerization and blending methods have been used for modifying their degradability and mechanical properties.[1,2] Recently, the ionomer concept has come to the field of degradable polyesters for properties modification.[3] An ionomer is defined as an ion-containing polymer with low mol % of ionic groups along the polymer backbone chains or as pendant groups. The introduction of an ionic unit into the polymer chain leading to clustering significantly alters its physical properties, such as enhanced mechanical properties, high melt viscosity, increased thermal stability, and altered degradability characteristics. Only a little is known about the degradable polyester-based ionomers. The known degradable polyester ionomers based on poly(L,L-lactide) (PLLA) and poly(caprolactone) PCL were synthesized by titrating aqueous LiOH, RbOH, CsOH, and KOH with the corresponding polymers with the COOH end groups.[4,5] In an another approach, polyester-based random ionomer is generated in which the ionic species are randomly distributed along the chain. They are made via conventional two-step polycondensation using adipic/succinic acid and 1,4-butylenediol in presence of dimethyl 5-sulfoisophthlate.[6,7]

In this work, we would like to present a new concept for the formation of degradable PCL-based ionomers. Conventional methods of making degradable polyesters are either by condensation polymerization of diols and diacids or cationic/anionic/metal-catalyzed ROP of cyclic esters. Another route to the synthesis of polyesters, in general, is also by using radical chemistry and is by radical ring-opening polymerization of cyclic ketene acetals (CKAs) as first shown by Bailey et al.[8] In past few years we have investigated this route for making polyesters and used it for making a new class of polymers called poly(vinyl-*co*-ester)s.[9−15] Using this method, free radical ring-opening polymerization of CKA, 2-methylene-1,3-dioxepane (MDO), gives polycaprolactone. The synthesis of PCL-based ionomers is carried out in two steps, i.e., radical ring-opening copolymerization of MDO with methyl methacrylate (MMA) *N,N*-dimethylaminoethyl methacrylate (DMAEMA) and subsequent quaternization with alkyl halides as shown in the Scheme 1. This opens a new field of making cationic ionomers in simple way. Structural characterization and properties evaluation of the resulting degradable materials by X-ray, dynamical mechanical analysis, and degradability studies in compost are also reported.

Experimental Section

Materials. *N,N*-Dimethylaminoethyl methacrylate (DMAEMA) (Acros) was distilled before use. Azobis(isobutyronitrile) (AIBN) was recrystallized from methanol prior to use. 2-Methylene-1,3-dioxepane (MDO), bromoethane (Acros), and 1-bromododecane

Scheme 1. Synthesis of PCL-Based Degradable Cationic Ionomers



---

* Corresponding author: e-mail seema@chemie.uni-marburg.de; Fax +4964212825755.

10.1021/ma802615f CCC: $40.75

Table 1. Bulk Terpolymerization of 2-Methylene-1,3-dioxepane (MDO), Methyl Methacrylate (MMA), and *N,N*-Dimethylaminoethyl Methacrylate (DMAEMA) (D) with 1 mol % of Azobis(isobutyronitrile) (AIBN) as Initiator[a]

	feed ratio (molar ratio)				terpolymer composition (molar ratio)				
run	MDO	MMA	D	yield (%)	MDO	MMA	D	M_n	PDI
1	30	65	5	81	12	81	7	37 000	2
2	50	45	5	70	21	69	10	55 000	2
3	70	25	5	64	40	50	10	−	−
4	70	20	10	52	40	40	20	−	−
5	70	15	15	49	40	32	28	−	−

[a] Reaction temperature: 70 °C; reaction time: 20 h; −: no signal generated by gel permeation chromatography (GPC).

(Acros) were used as received. Hexane (BASF), diethyl ether, chloroform, methanol (BASF), ethanol (BASF), dimethylformamide (DMF), and methyl methacrylate (MMA) (BASF) were distilled before use. THF was purified by distillation over potassium.

Instrumentation. ^1H (400.13 MHz) and ^{13}C spectra were recorded on a Bruker DRX-300 spectrometer in $CDCl_3$. Tetramethylsilane (TMS) was used as an internal standard.

The molecular weights of the polymers were measured at room temperature by gel permeation chromatography (GPC) using a Knauer system equipped with two columns, PSS-SDV (linear, 10 mL, 60 cm × 0.8 cm), a UV photometer, and a differential refractive index detector. DMF was used as eluent at a flow rate of 0.8 mL/min. A poly(methyl methacrylate) (PMMA) calibration was employed as a reference.

Dynamic mechanical analysis (DMA) was performed using a Perkin-Elmer Pyris diamond analyzer with a heating rate at 5 °C min^{-1} in a nitrogen atmosphere. The applied frequency and amplitude were respectively 1 Hz and 20 μm. The storage modulus (E'), loss modulus (E''), and loss tangent (tan δ) of the polymer film were recorded in the temperature range from −100 to 150 °C.

The tensile testing was performed using Instron tensile tester. The extension was applied at 30 cm/min at room temperature.

Small-angle X-ray scattering (SAXS) measurement was performed with a compact Kratky camera from Anton Paar and a detector PSD 50 from Firm Braun. The distance between the sample and the detector is 25 cm. The wavelength of the primary X-ray beam is 0.3 nm. The scattering angle (2θ) was performed from 0° to 10°. The average measuring time was set to be 1 h. Sample films were wrapped with aluminum folia and measured under a certain temperature. Besides the scattering peaks, most of the measurements generated one peak from the penetrated primary beam with q value around 0.1 nm^{-1}.

Transmission electron microscope (TEM) pictures were taken with a high-resolution transmission electron microscope of type JEM 3010 from JEOL equipped with a digital camera of 2000 × 2000 pixels under acceleration voltage of 300 kV. The thin film of polymer was made first by dissolving ionomer in $CHCl_3$ and then dipping the TEM grid once fast in the solution, followed by drying the grid under air.

Biodegradability Test. Cationic ionomers film (10 cm × 2 cm × 0.1 mm) with 40 mol % of MDO and up to 12 mol % of quaternary amine were made by a compression-molding machine. Such polymer film was buried in compost (BASF) under 60 °C for different time intervals.

Synthesis of Poly(MDO-*co*-MMA-*co*-DMAEMA). In general, all terpolymerization reactions were carried out under argon in predried Schlenk tubes using free radical initiator AIBN. In a typical polymerization reaction, MDO (0.77 g, 7 mmol), MMA (0.250 g, 2.5 mmol), and DMAEMA (0.079 g, 0.5 mmol), in a molar ratio of 70:25:5 and 1 mol % of the total monomers of the initiator AIBN were placed in a Schlenk tube under argon. Small residual O_2 was removed from the tube by one freeze−cooling−thaw cycle. Then the reaction was started by placing the reaction tube in a preheated oil bath at 70 °C. After 20 h polymerization, the reaction mixture was diluted with $CHCl_3$ and precipitated in about 200 mL of *n*-hexane. Purification of the polymers was done by dissolving in $CHCl_3$ and reprecipitation in *n*-hexane. The terpolymers were dried in vacuum at 40 °C until constant weight. The microstructure of the terpolymer was characterized by ^1H NMR techniques. Different terpolymers of MDO, MMA, and DMAEMA were made by changing the molar ratio of the monomers in the initial feeds under similar reaction conditions as described above (Table 1).

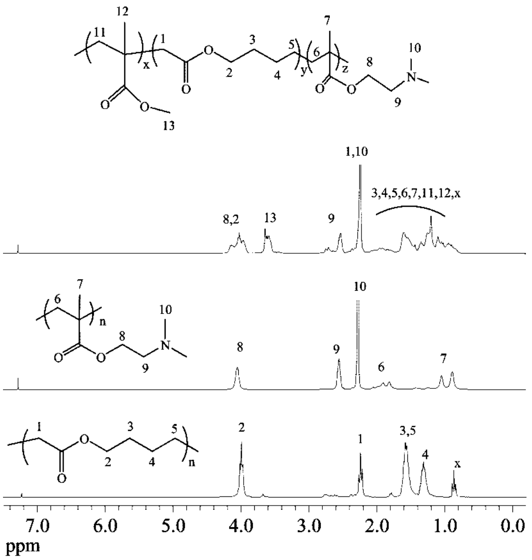


Figure 1. ^1H NMR spectrum of P(MDO-*co*-MMA-*co*-DMAEMA) with the initial feed of MDO:MMA:DMAEMA = 1:1:1 in $CDCl_3$.

Quaternization of Poly(MDO-*co*-MMA-*co*-DMAEMA). 500 mg of poly(MDO-*co*-MMA-*co*-DMAEMA) was well dissolved in 50 mL of chloroform at RT. Then around 60 mmol of alkyl bromide was added to the mixture. Quaternization reaction underwent for 3 days by stirring and heating at 40 °C in the oil bath. The solvent was removed under vacuum. Purification was done by dissolving the resulting ion-containing polymer in chloroform and reprecipitation in *n*-hexane. The quaternization conversion was quantitatively determined with elemental analysis by comparing the molar amounts of bromide and nitrogen.

Results and Discussion

Copolymerization and Quaternization. Degradable ionomers were synthesized by free-radical ring-opening terpolymerization of 2-methylene-1,5-dioxepane (MDO) with other vinyl monomers like methyl methacrylate (MMA) and *N,N*-dimethylaminoethyl methacrylate (DMAEMA), followed by quaternization of DMAEMA with alkyl bromides like ethyl bromide (Scheme 1). Different copolymers were made by changing the molar ratio of the three monomers MDO, MMA, and DMAEMA in the feed. The representative ^1H NMR of the copolymers with an initial feed of MDO:MMA:DMAEMA as 1:1:1 (molar ratio) is shown in Figure 1. It showed all the characteristic peaks from MDO, MMA, and DMAEMA, indicating the existence of the termonomers in the copolymers (Figure 1). The signal at 0.85 ppm and other small signals in ^1H NMR are due to the well-known back-biting reactions occurring simultaneously with radical ring-opening polymerization of MDO and are analyzed in detail in our previous publication.[9] The terpolymer composition was determined by using the peak intensities at 3.7 ppm [I_{MMA} ($-COOCH_3$, proton

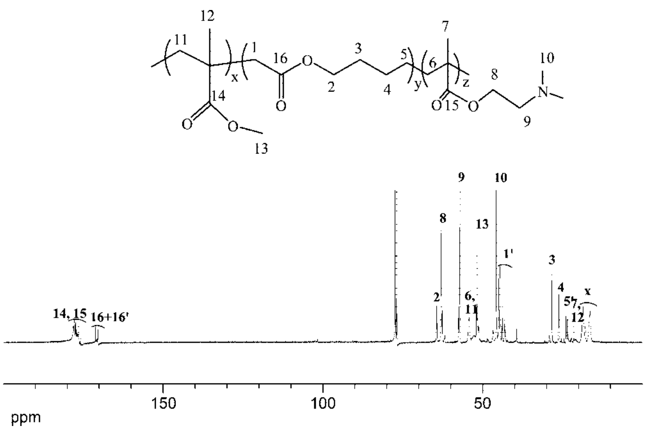


Figure 2. ^{13}C NMR spectrum of P(MDO-*co*-MMA-*co*-DMAEMA) with the initial feed of MDO:MMA:DMAEMA = 1:1:1 in $CDCl_3$.

Table 2. Kinetic Information on Copolymerization of 2-Methylene-1,3-dioxepane (MDO), Methyl Methacrylate (MMA), and *N*,*N*-Dimethylaminoethyl Methacrylate (DMAEMA) (D) (50:25:25 mol % in the Initial Feed)[a]

run	reaction time (h)	terpolymer composition (molar ratio)			total conversion (%)
		MDO	MMA	DMAEMA	
1	1/6	9	45	46	12
2	2/3	12	44	44	46
3	1.5	20	42	38	70
4	4	21	43	36	73
5	15	21	38	41	74

[a] AIBN:monomers = 1:100 (in molar ratio); copolymerization temperature: 70 °C.

13 of PMMA)], 2.3 ppm [I_{DMAEMA} ($-CH_2CH_2N-$, proton 9 of PDMAEMA)], and 4.2−3.8 ppm [$I_{\mathrm{MDO}} + I_{\mathrm{DMAEMA}}$ ($-CH_2CH_2N-$, proton 8 of PDMAEMA + $-OCH_2CH_2-$, proton 2 of PMDO)] and was found to be MDO:MMA:DMAEMA = 12:43:45. Similarly, copolymer composition is determined for other tercopolymers and is tabulated in the Table 1. The amount of MMA and DMAEMA in the terpolymers was found to be always higher than that in the initial feed. The terpolymers with increased amount of ester linkages could be produced in a simple way just by increasing the amount of MDO in the initial feed. ^{13}C NMR (Figure 2) showed no signals around 110 ppm, thereby showing the absence of acetal linkages and shows the complete ring-opening reaction of MDO during copolymerizations. Also, splitting of carbonyl peaks of monomers in the region 170−180 ppm showed randomization of the monomers during copolymerization. In order to have an insight into the copolymerization behavior and the microstructure of the copolymers, for one specific initial feed (MDO:MMA:DMAEMA = 50:25:25 molar ratio), the polymerization was followed at different intervals of time (Table 2). There was a continuous increase of reacted MDO, MMA, and DMAEMA with time, indicating a constant incorporation of all the monomers during the polymerization (Figure 3).

Molecular weights of terpolymers were measured by GPC (Table 1). Generally, terpolymers showed unimodal peak with a molecular weight around 30 000−60 000 (Figure 4) and a typical polydispersity around 2.0. Some of the samples of terpolymers did not generate visible signals in the GPC curves (DMF as solvent). Problem may result from the interaction of terpolymers with the column. The reason for this is not yet clearly known.

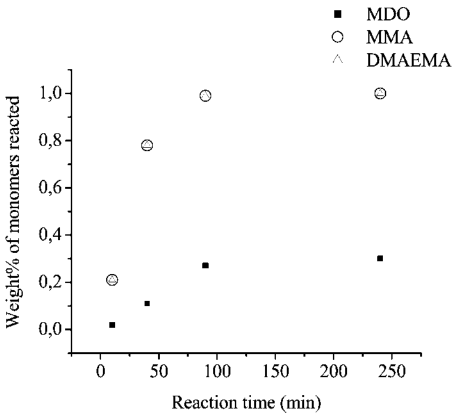


Figure 3. Weight % of reacted monomers (wt % of the monomer based on the quantity at the beginning has reacted) versus reaction time. Monomers in initial feed: MDO:MMA:DMAEMA = 50:25:25 (mol %); AIBN: monomers = 1:100 (mol %), reaction temperature: 70 °C.

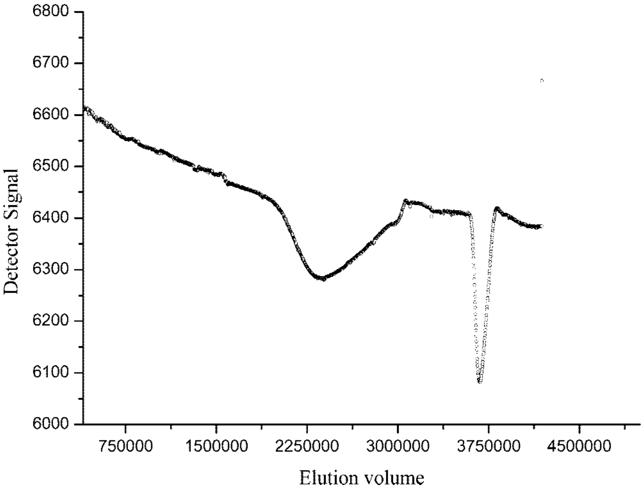


Figure 4. GPC curve of P(MDO-*co*-MMA-*co*-DMAEMA) (run 1, Table 1).

Polymerization was followed by quaternization of amines in DMAEMA units of terpolymers with ethyl bromide (Table 3). Quaternization was carried for 3 days to get a relative high conversion which was determined by elemental analysis by comparing the mol % of bromine and nitrogen in the samples (conversion = mol % Br/mol % N). Polymers with 40 mol % of ester groups and different amount of quaternary amine based on BrC_2H_5 were generated.

Ionic Aggregation Behavior. For most of the widely investigated anionic ionomers, like poly(styrene-*co*-sodium methacrylate), two kinds of ionic environments (primary and higher aggregates) were detected in ionomers by several spectroscopic experiments.[16,17] Several models have been proposed for this phenomena, including the core−shell model, the hard-sphere model, and the most popular multiplet-cluster model. Based on Eisenberg model, the formation of primary ionic aggregates, known as multiplets, is the fundamental element in ionomers. Because of the dramatic difference of the solubility and the size between the ion pairs (such as $-COO^-Na^+$ or $-SO_3^-Na^+$) and the nonionic polymer segments, only several (no more than 10) ion pairs can possibly associate together to form a multiplet, which is tightly attached and separated with each other by the long neutral polymer chains. At higher ionic content, several multiplets together with their nonionic surrounding will overlap to form higher aggregate regions, which are called clusters. The characteristic anionic ionomer SAXS peaks, centered at q values ranging from 1.5 to 2.5 nm^{-1}, result from scattering of the primary multiplets. The scattering spaces ranging from 4 to 2.5 nm, based on Bragg's law ($d = \lambda/2 \sin \Theta$), are assigned to be the distances between

Table 3. Quaternization of P(MDO-*co*-MMA-*co*-DMAEMA[a]

	terpolymer composition (molar ratio)			quaternization		
run	MDO	M	D	BrC_nH_{2n+1}	conversion (%)	ion content (mol %)
1	40	50	10	2	91	9
2	40	40	20	2	95	19
3	40	32	28	2	96	27

[a] Reaction time: 3 days (ion content was calculated by “mol % of DMAEMA in polymer” × “quaternization conversion”).

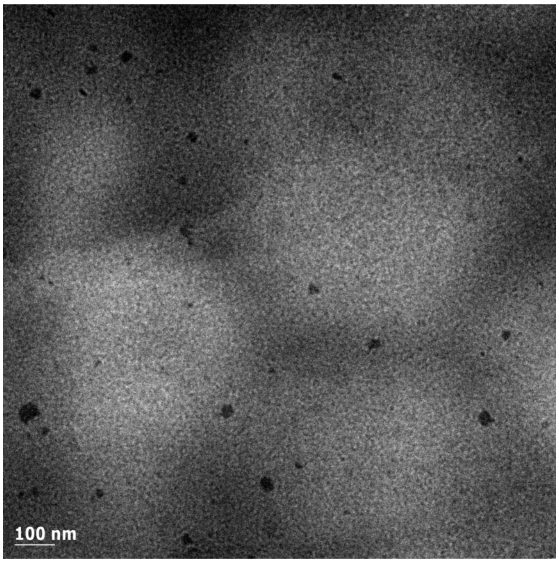


Figure 5. TEM pictures of P(MDO-*co*-MMA-*co*-DMAEMA)·BrC_2H_5 containing 9% ion (40−50−10); sample prepared by film casting on the TEM grid.

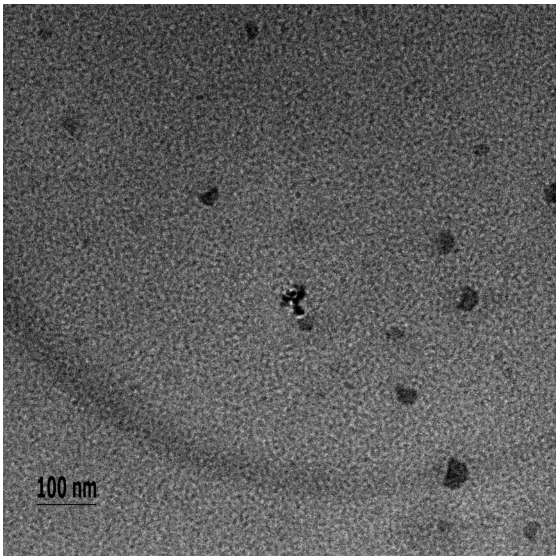


Figure 6. TEM pictures of P(MDO-*co*-MMA-*co*-DMAEMA·BrC_2H_5 containing 18% ion (40−40−20); sample prepared by film casting on the TEM grid.

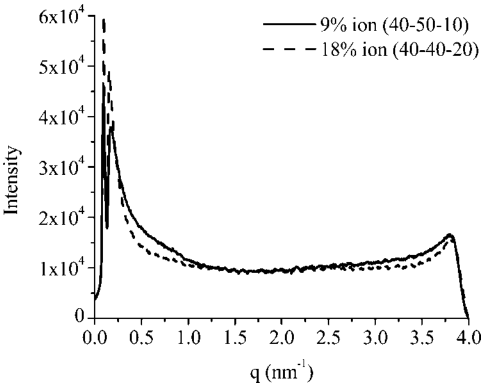


Figure 7. SAXS profile of P(MDO-*co*-MMA-*co*-DMAEMA·BrC_2H_5).

multiplets. However, the cationic ionomers, which were studied here, are found to be a different system from the well-known anionic ionomers.

Because of the big molar mass of bromine, the counterion, and the high ionic aggregate regions in the ionomers could be directly observed by TEM. Figures 5 and 6 clearly show the visible ionic aggregates with a diameter concentrated around 30 nm. Precisely, there seems to be an amount of finely small aggregates and, therefore, a broad distribution of the sizes, which could not be seen very clearly due to the limited resolution of the TEM technique. The sizes of the visible aggregates in TEM pictures were almost similar when the total ionic amount increased to twice, i.e., from 9 to 18 mol %. The form of the observed aggregates was irregular from the first sight. However, Figure 5 showed that the aggregates tend to grow to be spherical. TEM pictures cannot give a clue of distances between the aggregates or the density of the aggregates in the ionomers since the thicknesses of the films prepared for TEM are not identical and the resolution of TEM is limited. More detailed information about the morphology, including the distance of the aggregates, the formation of the aggregates, and the possibility of the existence of the two kinds of ionic aggregates, etc., was investigated using small-angle X-ray scattering (SAXS). SAXS analysis has been actually the most reliable and the most available evidence for the existence of the ionic aggregates in ionomers. A peak was observed in SAXS profile (Figure 7) for polymers with 9% and 18% ionic groups, resulting from the scattering of ionic aggregates. The scattering peak was much broad and centered at $q = 0.16\ nm^{-1}$. Based on Bragg’s law ($d = \lambda/2 \sin \Theta$), there was a broad distribution of the scattering spaces, ranging from 5 to 45 nm and centered at 36 and 40 nm for 9% and 18% of ion, respectively. This average space was in the order of the size of the aggregates, which is around 30 nm, observed by TEM techniques. It is proposed that the characteristic SAXS peak with a q value centered at $0.16\ nm^{-1}$ does not derive from the scattering of primary multiplets, but direct from higher ionic aggregates (30 nm), called clusters, and the scattering spaces were assigned to be the distances between clusters. When increasing the amount of the total ion content from 9% to 18%, the intensity of the scattering peaks increased, which indicates an increase of the surface area of the clusters.

Dynamic mechanical analysis (DMA) is a very useful method to further explore the properties of the ionic aggregates and the nonionic polymer backbones, including the sizes, the volume fraction of the aggregates, and the restricted mobility of the chains of ionomers. The dynamic properties of ionomers quaternized with BrC_2H_5 are shown in Figure 8. Nonionic poly(MMA-*co*-MDO-*co*-DMAEMA) showed one peak centered at 41 °C, which showed the glass transition of the nonionic polymer chains. In ionomers quaternized with BrC_2H_5 with 9% of ionic groups, there was one peak for glass transition at 51 °C and a clear shoulder around 80 °C. Because of ionic

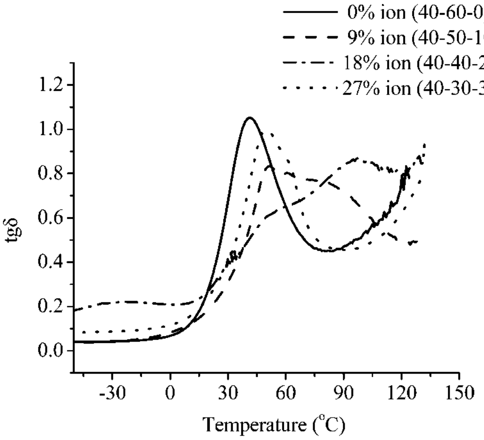


Figure 8. Loss tangent (tg δ) vs temperature of P(MDO-*co*-MMA-*co*-DMAEMA·BrC_2H_5).

aggregates, the mobility of the nonionic polymer backbones was also restricted. Therefore, the glass transition temperature increased by 10 deg. The shoulder at 80 °C resulted from the glass transition temperature of the ionic aggregates with highly restricted mobility. As is known, once a region can show a separated glass transition, the size of it should be at least 5−10 nm.[18] Therefore, the majority of the sizes of the ionic aggregates should be more than 5−10 nm, which is in agreement with the proposals according to TEM and SAXS analysis. These aggregates are what we called clusters. When ionic content increased to 18%, the shoulder increased further to 97 °C and became a clear peak. As is known, the areas of the peaks indicate the volume fractions of the nonionic polymer regions between aggregates and ionic aggregates regions. Even though the quantitative data could not be calculated due to the peak overlapping, it can be seen that the volume fraction of the ionic aggregates increased greatly when increasing the total ionic content from 9% to 18%. The increasing ionic content increased the glass transition of both the matrix polymer chains and also the ionic aggregate regions. However, the dielectric constant of the matrix polymer chains influenced the formation of ionic aggregates. When the total ionic content further increases to 27%, the higher glass transition temperature disappeared, and there is again one peak around 51 °C. Clearly there is no big ionic aggregate existing in this polymer. It indicates that there is a limit of ionic content for ionomers quaternized with BrC_2H_5 to generate higher ionic aggregates, which are more than 5−10 nm. When the ionic content exceeded the limit leading to a high dielectric constant of the whole polymers, the ionic groups tend to be dissolved in the whole polymer, probably leading to no aggregations and therefore no ionomeric effects.

Because of the formation of ionic aggregates, the shapes of storage modulus versus temperature for different polymers changed (Figure 9). The storage moduli of different polymers at low temperatures up to 0 °C are similar, without visible influence from the ionic aggregates. When temperature increased close to the glass transition of the matrix polymer around 30−40 °C, due to the formation of the ionic aggregates, the storage modulus of ionomers became higher than nonionic poly(MMA-*co*-MDO-*co*-DMAEMA). Increasing the ionic amount from 9% to 18%, the storage modulus increased to some extent, indicating the increase of ionic aggregates. The storage modulus of P(MDO-*co*-MMA-*co*-DMAEMA·BrC_2H_5 with 27% of ion decreases compared to ionomers with 9% and 18% of ion, again indicating the decrease of ionic aggregates.

The mechanical properties of the new materials are studied using a conventional tensile testing machine. The ionic aggregates in ionomers quaternized with BrC_2H_5, which can show a separated glass transition, increased the Young's modulus dramatically (Table 4). When increasing the amount of ion from 9% to 18%, the Young's modulus increased, and the elongation and the maximum stress do not change much considering the experimental errors. In general, they showed an elongation of about 200−250%. Suppose the ionic aggregates mainly act as fillers in the ionomers quaternized with BrC_2H_5. According to the equation for the filler systems $E^* = E(1 + 2.5V_f + 14.1V_f^2)$,[19] where E^* stands for Young's modulus of filled system, E stands for Young's modulus of unfilled system, and V_f stands for the volume fraction of the filler, it is possible to calculate the volume fraction of the ionic aggregates in ionomers (Table 4). Increasing the ionic amount from 9% to 18%, the calculated volume fraction of ionic aggregates increased from 47% to 61%. Ionomer with 27 mol % of ionic groups showed a decrease in the volume fraction of ionic aggregates from 61% to 40%, indicating the tendency of dissociation of ionic aggregates by high ionic amount for polymers quaternized with bromoethane. This could also be noticed from the decrease in modulus and strength on increasing the ionic content.

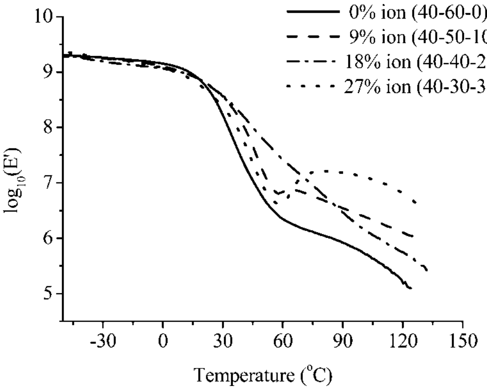


Figure 9. Log (E') vs temperature for P(MDO-*co*-MMA-*co*-DMAEMA·BrC_2H_5.

Table 4. Mechanical Properties of Quaternized P(MDO-*co*-MMA-*co*-DMAEMA Containing 40% of MDO and Different Types of Ionic Groups[a]

polymer	max STR (MPa)	max STN (mm/mm)	modulus (MPa)	V_f (%)
(40−60−0), 0% ion	15.7	4.5	74.1	0
(40−50−10, 2), 9% ion	16.6	2.3	390.9	47
(40−40−20, 2), 18% ion	15.4	2.0	577.3	61
(40−30−30, 2), 27% ion	13.32	1.7	312.8	40

[a] (40−50−10, 2) means polymer with MDO:MMA:DMAEMA = 40:50:20 in molar ratio quaternized with BrC_2H_5; V_f: volume fraction of ionic aggregates, calculated based on filler theory.

The driving force of the firm and even spherical primary ionic aggregates, known as multiplet, is the high ion−counterion electrostatic association energy and the dramatic difference of the solubility of the ionic groups from the polymer chains. Considering the structural characteristic of this quaternary amine−cationic ionomer system, the strength of ionic association energy and the difference of the solubility between ionic groups and the polymer backbones are highly decreased by the alkyl groups (including two methyl groups and one ethyl group) on the quaternary amines. It is therefore not possible to form a sharp interface between ionic groups and nonionic polymer chains. Because of the relative weak ionic association energy, the primary multiplets may contain less number of ionic groups than that in anionic ionomers. At a higher ionic content, the distances between multiplets decreases. Once overlapping of the restricted polymer covers surrounding the multiplets take place, primary multiplets tend to form higher aggregates, called clusters. When the quaternization takes place, it is not perfectly random; there is supposed to be a broad distribution of the sizes

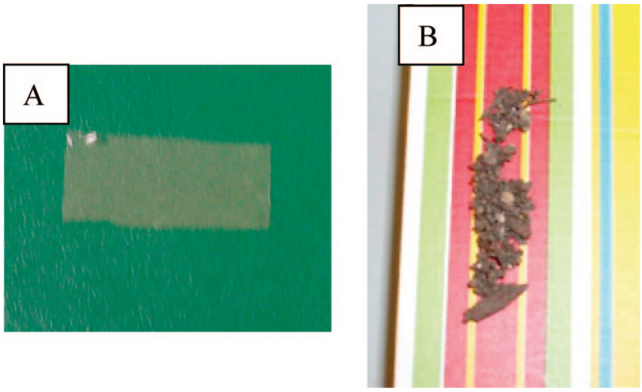


Figure 10. Poly(MDO-*co*-MMA-*co*-DMAEMA$\cdot$BrC$_2$H$_5$ containing 40 mol % of MDO and 12 mol % of ion: (A) original sample; (B) 2 weeks after buried in compost.

of the multiplets and also clusters. If the weak multiplets intracluster can scatter X-rays, the q value may too high and beyond the experimental range, which is 0−4 nm^{-1}. The scattering ionic peak with a q value centered at 0.16 nm^{-1} results from the scattering of higher aggregates, called clusters. The scattering spaces were assigned to be the distances between clusters. TEM could not show a clear difference between the sizes of the aggregates with increasing the ionic content from 9% to 18%, partly due to the resolution of the techniques. Another reason could be a balance between electrostatic energy of the ionic association and the elastic energy of the nonionic polymer chains was achieved for the size of aggregates at such high ionic contents. Therefore, the size of the ionic aggregate is limited. In fact, the intensity of the scattering peak increased greatly. It indicates that the concentration of the aggregates increases with increasing the ionic content. From X-ray profile we also can see the scattering intensity from the short scattering distances (around 5−15 nm) decreases somehow, which may indicate that the very small aggregates grow to bigger ones.

Preliminary degradability studies are also carried out in compost and showed highly encouraging results. 0.1 mm thick ionomer P(MDO-*co*-MMA-*co*-DMAEMA$\cdot$BrC$_2$H$_5$) film containing 40 mol % of MDO and 12 mol % of ion was buried in compost under proper humidity at 60 °C. Visible degraded holes were found out after 2 weeks, demonstrating the biodegradability of the ionomers (Figure 10).

Conclusion

Successful synthesis of PCL-based degradable ionomers using free radical chemistry is shown for the first time. These degradable ionomers P(MDO-*co*-MMA-*co*-DMAEMA$\cdot$BrC$_2$H$_5$ were synthesized by random radical terpolymerization of MDO, MMA, and DMAEMA and subsequent quaternization. The strength of ionic association differs with different amounts of ionic moieties. Ionomers quaternized with BrC$_2$H$_5$ generate ionic aggregates with a diameter around 30 nm. The higher ionic aggregates act in polymer as fillers to increase the Young's modulus dramatically. Ionomers with 40 mol % of MDO and 12 mol % of quaternary amine showed biodegradability in compost. This opens a new field of making degradable ionomers using free-radical polymerization. Further, it would be interesting to achieve physical cross-linking from the ionic clusters instead of acting as filler, and work in this direction is in progress in our laboratory.

References and Notes

(1) Ishida, K.; Wang, Y.; Inoue, Y. *Biomacromolecules* **2001**, *2*, 1285–1293.
(2) Kasperczyk, J. *Macromol. Symp.* **2001**, *175*, 19–32.
(3) Han, S. I.; Yoo, Y.; Kim, D. K.; Im, S. S. *Macromol. Biosci.* **2004**, *4*, 199–207.
(4) Sherman, J. W.; Storey, R. F. *Polym. Prepr.* **1998**, *39*, 602.
(5) Storey, R. F.; Sherman, J. W. *Polym. Prepr.* **1996**, *37*, 624.
(6) Yoo, Y. T.; Lee, B. J.; Han, S. I.; Im, S. S.; Kim, D. K. *Polym. Degrad. Stab.* **2003**, *79*, 257.
(7) Han, S. I.; Im, S. S.; Kim, D. K. *Polymer* **2003**, *44*, 7165–7163.
(8) Bailey, W. J.; Ni, Z.; Wu, S. R. *J. Polym. Sci., Polym. Chem.* **1982**, *20*, 3021.
(9) Agarwal, S. *Polym. J.* **2006**, *39*, 163.
(10) Ren, L.; Speyer, C.; Agarwal, S. *Macromolecules* **2007**, *40*, 7834–7841.
(11) Ren, L.; Agarwal, S. *Macromol. Chem. Phys.* **2007**, *208*, 245−253.
(12) Agarwal, S. *J. Polym. Res.* **2006**, *13*, 403–412.
(13) Lutz, J.-F.; Andrieu, J.; Uzgun, S.; Rudolph, C.; Agarwal, S. *Macromolecules* **2007**, *40*, 8540–8543.
(14) Wickel, H.; Agarwal, S.; Greiner, A. *Macromolecules* **2003**, *36*, 6152–6159.
(15) Wickel, H.; Agarwal, S. *Macromolecules* **2003**, *36*, 2397–2403.
(16) Hodge, I. M.; Eisenberg, A. *Macromolecules* **1978**, *11*, 289–293.
(17) Andreeva, E. D.; Nikitin, V. N.; Bovartchuk, Yu. M. *Macromolecules* **1976**, *9*, 238–243.
(18) Eisenberg, A.; Hird, B.; Moore, R. B. *Macromolecules* **1990**, *23*, 4098–4107.
(19) Guth, E. *J. Appl. Phys.* **1945**, *16*, 20.

MA802615F