Available online at www.sciencedirect.com
SCIENCE DIRECT
Polymer 46 (2005) 11698–11706
polymer
www.elsevier.com/locate/polymer

# Synthesis and characterization of copolymers of 5,6-benzo-2-methylene-1,3-dioxepane and *n*-butyl acrylate

Jinyu Huang, Roberto Gil, Krzysztof Matyjaszewski *

*Department of Chemistry, Center for Macromolecular Engineering, Carnegie Mellon University, 4400 Fifth Avenue, Pittsburgh, PA 15213, USA*

Received 4 July 2005; received in revised form 11 September 2005; accepted 13 September 2005
Available online 15 October 2005

**Abstract**

The ATRP copolymerization of 5,6-benzo-2-methylene-1,3-dioxepane (BMDO) with *n*-butyl acrylate (*n*BA) was studied by using ethyl 2-bromoisobutyrate (EBriBu) and *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA)/Cu(I)Br as the initiator and catalyst, respectively. The reactivity ratios of the monomers in the copolymerization were determined using the Kelen–Tüdõs method and were found to be $r_{BMDO}=0.08$ and $r_{nBA}=3.7$. The copolymer yield decreased with higher amounts of BMDO in the initial feed. The structure of these copolymers was thoroughly characterized by 1D and 2D NMR techniques and quantitative ring opening of BMDO in its copolymerization was demonstrated. The hydrolytic degradation behavior of the BMDO/*n*BA copolymers was also studied.
© 2005 Elsevier Ltd. All rights reserved.

*Keywords:* Radical ring-opening polymerization; Reactivity ratio; Hydrolytic degradation

## 1. Introduction

A wide variety of biodegradable polymers were developed and used as biomaterials for drug delivery systems [1], scaffolds for tissue engineering [2], gene vectors [3], or sutures [4]. Aliphatic polyesters [5] such as poly(lactic acid), poly(glycolic acid), and poly(ε-caprolactone) are among the most prevalent biodegradable polymers in those applications. Polycondensation, ionic and coordination ring-opening polymerizations were employed as the basic methods for the preparation of aliphatic esters [6]. However, these methods suffer from some shortcomings. For polycondensation, high temperature, long reaction time, removal of reaction by-products, and a precise stoichiometric balance are needed to obtain high molecular weight polymers. For ionic or coordination ring-opening polymerizations, stringent purification is required.

Radical ring-opening polymerizations (RROP) [7] have attracted significant research interest because they overcome many of the shortcomings described above and could provide a convenient synthetic route to polymers with cleavable groups in the backbone. Additionally, the use of ring-opening polymerization may minimize the volume shrinkage that usually occurs during polymerization [8]. Significant research has been done on RROP of cyclic ketene acetals such as 2-methylene-1,3-dioxepane (MDP) [9], 5,6-benzo-2-methylene-1,3-dioxepane (BMDO) [10], and 2-methylene-1,3,6-trioxocane (MTC) [11]. The introduction of ester or ester–ether linkages in the polymer backbone renders the resulting polymers hydrolytically, photo- or biodegradable. However, the polymers obtained by conventional radical polymerization generally have uncontrolled molecular weight and broad molecular weight distribution.

By utilizing the recently developed controlled/living radical polymerization (CRP) techniques [12], the synthesis of degradable copolymers with controlled molecular weight and narrow molecular weight distribution through RROP becomes possible. This was demonstrated by the controlled RROP of MDP using stable free radical polymerization (SFRP) [13] and reversible addition-fragmentation transfer polymerization (RAFT) [14] and BMDO via atom transfer radical polymerization (ATRP) [15].

Due to poor physical properties of the homopolymers of cyclic acetals, they have not found practical application. However, copolymerization with other monomers could allow for the production of materials with desirable properties.

Recent reports on copolymerization of BMDO with styrene (S) or methyl methacrylate (MMR) through ATRP demonstrated the possibility to prepare hydrolytically degradable S/BMDO and MMA/BMDO copolymers with defined

* Corresponding author. Tel.: +1 412 268 3209; fax: +1 412 268 2897.
*E-mail address:* km3b@andrew.cmu.edu (K. Matyjaszewski).

0032-3861/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2005.09.048

structures and relatively narrow molecular weight distributions [15,16]. The introduction of ester groups into the copolymer, however, was not very efficient since BMDO is much less reactive than those vinyl monomers. Two strategies have been attempted to enhance the incorporation of the cyclic monomer into the copolymers by using either more reactive cyclic monomer or vinyl comonomer with the higher cross-propagation tendency.

We previously reported copolymerization of MMA with 5-methylene-2-phenyl-1,3-dioxolan-4-one (MPDO) with efficient incorporation of MPDO via ATRP [17]. The evidence of ring opening of MPDO in this copolymerization was drawn solely based on the degradation experiments. However, more detailed spectroscopic studies indicated that copolymerizations occurred predominantly through vinyl addition rather than ring opening [18]. Since BMDO is a nucleophilic monomer, copolymerization of BMDO with *n*-butyl acrylate (*n*BA), which produces more electrophilic radicals in comparison with S or MMA, should be more promising.

This paper explores the copolymerization behavior of BMDO with *n*BA as a comonomer using ethyl 2-bromoisobutyrate (EBriBu) and Cu(I)Br/*N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA) as the initiator and catalyst, respectively. The structural characterization of resulting copolymers using 1D and 2D NMR spectroscopy and the hydrolytic degradation of BMDO/*n*BA copolymers is reported.

## 2. Experimental section

### 2.1. Materials

All chemicals were obtained from Aldrich unless otherwise stated. Tetrahydrofuran (THF) was purified by distillation over sodium. *n*-Butyl acrylate (*n*BA, 99%) was stirred over $CaH_2$ overnight and distilled under reduced pressure. Dimethyl phthalate (99%), lithium aluminum hydride (95%), potassium *tert*-butoxide (95%), sodium carbonate (99.5%), sodium bicarbonate (99%), anhydrous magnesium sulfate, *p*-toluenesulfonic acid monohydrate (98.5%), chloroacetaldehyde dimethylacetal (98%), ethyl 2-bromoisobutyrate (EBriBu, 98%), and sulfuric acid were used as received. Copper (I) bromide (98%) was purified by stirring in glacial acetic acid overnight, filtering, and washing with dry ethanol. *N*,*N*,*N*′,*N*″,*N*″-Pentamethyldiethylenetriamine (PMDETA, 99%) was purified by passing through a neutral alumina column before use.

5,6-Benzo-2-methylene-1,3-dioxepane (BMDO) were synthesized using the methods previously reported [19].

### 2.2. Homo- and copolymerization of BMDO with nBA

All homo- and copolymerization reactions were carried out under nitrogen in a Schlenk flask employing ATRP reaction conditions [20]. In a typical copolymerization reaction (run 4, Table 1), 1.5 g (9.24 mmol) of BMDO, 1.3 mL (9.24 mmol) of *n*BA, 38 μL (0.19 mmol) of PMDETA, and 38 μL (0.19 mmol) of EBriBu were added to a 10 mL Schlenk flask. After three freeze-pump-thaw cycles, Cu(I)Br (27.4 mg, 0.19 mmol) was added under $N_2$. After stirring for 10 min at room temperature (rt), the flask was placed in a thermostated oil bath at 110 °C. Samples were taken to analyze the monomer conversion by $^1$H NMR spectroscopy and the molecular weight by GPC at different time intervals during the polymerization. The polymerization was stopped by cooling to room temperature and opening the flask to air. The mixture was then diluted with 10 mL THF and passed through a small neutral alumina column. The final pure product was obtained after precipitating into hexanes. Various copolymers of BMDO and *n*BA were prepared by changing the molar ratio of the two monomers in the feed under reaction conditions similar to those described above. Details of the reaction conditions with monomer feed ratios and results are given in Table 1.

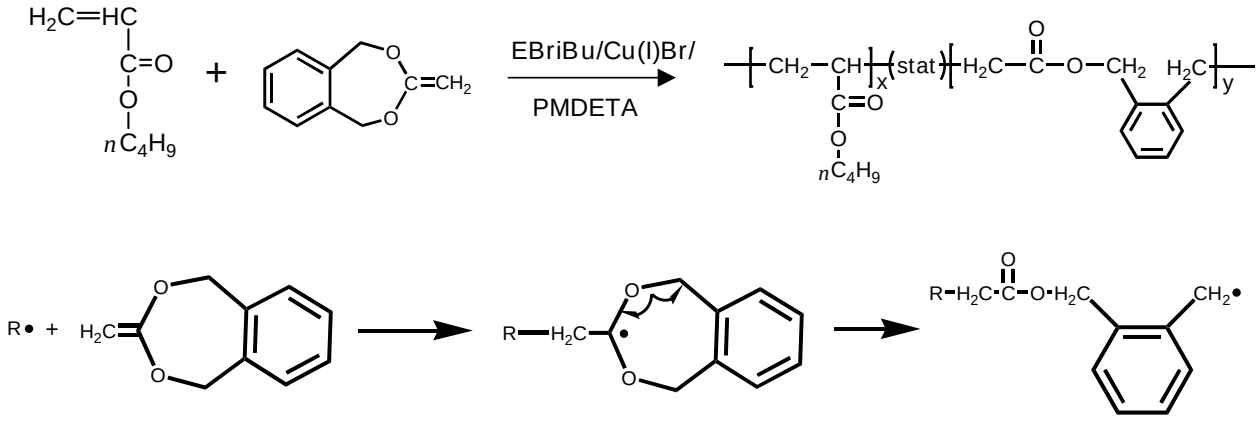
### 2.3. Hydrolysis of BMDO/nBA copolymer

Fifty milligram of copolymer (entry 6, Table 1) was dissolved in a solution of THF (3 mL) and 1-butanol (2 mL) in a 20 mL vial. After adding two drops of concentrated sulfuric acid, the mixture was heated to 80 °C. After 0.5 h, 1 mL of the mixture was taken and the solvent was removed under vacuum. The polymer sample was dissolved in chloroform. After extraction with a small amount of water, the organic phase was isolated, and the solvent was removed. The remaining polymer was analyzed by GPC.

Table 1
Copolymerization of BMDO with *n*BA

| Entries | *M* feed ratio (mol%) | | Time (h) | Yield (%) | $M_n$ (theo.) (g/mol) | $M_n$ (GPC) (g/mol) | PDI | Composition (mol%) NMR | |
|---|---|---|---|---|---|---|---|---|---|
| | BMDO | *n*BA | | | | | | BMDO | *n*BA |
| 1 | 100 | 0 | 48 | 20 | 3,200 | 3,800 | 1.74 | 100 | 0 |
| 2 | 80 | 20 | 20 | 31 | 4,400 | 5,200 | 1.84 | 48 | 52 |
| 3 | 70 | 30 | 18 | 33 | 4,600 | 7,500 | 1.65 | 40 | 60 |
| 4 | 50 | 50 | 20 | 52 | 7,300 | 11,300 | 1.66 | 28 | 72 |
| 5 | 30 | 70 | 22 | 67 | 11,600 | 15,200 | 1.54 | 19 | 81 |
| 6 | 20 | 80 | 22 | 67 | 12,000 | 20,500 | 1.60 | 11 | 89 |
| 7 | 0 | 100 | 1.4 | 87 | 11,100 | 12,200 | 1.18 | 0 | 100 |

$[EBriBu]_0$:$[M]_0$:$[Cu(I)Br]_0$:$[PMDETA]_0$ = 1:100:1:1, $T$ = 110 °C. EBriBu = ethyl 2-bromoisobutyrate, $M$ = monomers, PMDETA = *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine. The calculation of the polymer composition is based on the integral areas that are attributed to the $CH_2$ ($\delta$ = 5.1 ppm) of the BMDO unit and $CH_2O$ ($\delta$ = 4.0 ppm) of *n*BA.




Scheme 1. P(BMDO-*co*-*n*BA) synthesis via ATRP.

### 2.4. Analysis

Molecular weights were analyzed using GPC (Waters 717 Plus autosampler, four Polymer Standard Service columns in series (guard, $10^5$, $10^3$, 100 Å) and a Waters 410 differential refractometer). Toluene was used as the internal standard, and the molecular weights of copolymers were determined using linear polystyrene standards.

The NMR spectroscopy experiments were recorded on a Bruker Avance DMX-500 spectrometer operating at 500.13 MHz ($^1$H) and 127.76 MHz ($^{13}$C). The 1D $^1$H and 2D $^1$H–$^{13}$C correlation experiments (edited-HSQC and HMBC) were acquired in a 5 mm z-gradient Broad Band Inverse probe using Bruker standard pulse sequences provided with the XWIN-NMR 3.5 software package. The edited-HSQC experiment was recorded in echo–antiecho mode using the hsqcedetgp pulse program optimized for a C–H coupling constant of 145 Hz. Delay d21 was set to $1/(2J_{CH})=3.5$ ms for multiplicity selection: $CH_3$, CH positive, and $CH_2$ negative. The HMBC experiment was acquired in quadrate forward mode using the hmbcgplpndqf pulse program, with a low-pass filter of 145 Hz to suppress one-bond correlations, optimized for a long-range coupling of 8 Hz, and no decoupling during acquisition. 2D NMR spectroscopy data were acquired with 2048 points in t2, and the number of increments for t1 was 256. A relaxation delay of 1 s was used for all 1D experiments and 2 s for all 2D experiments. The 1D $^{13}$C NMR spectra were acquired in Bruker Avance AV-300 operating at 300.13 MHz ($^1$H) and 75.47 MHz ($^{13}$C) using a 5 mm z-gradient Broad Band Observe probe. All NMR spectroscopy experiments were processed and plotted using the XWIN NMR software.

## 3. Results and discussion

### 3.1. Simultaneous copolymerization

Copolymerization of BMDO and *n*BA was carried out under ATRP reaction conditions employing the EBriBu/Cu(I)Br/PMDETA initiating system (Scheme 1).

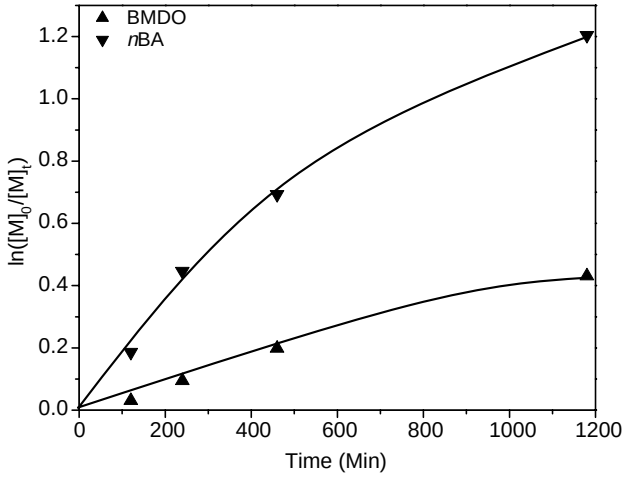



Fig. 1. The plot of the first-order monomer consumption vs. time for copolymerization at the molar ratio of BMDO:*n*BA = 1:1 (entry 4, Table 1). $[EBriBu]_0:[M_{BMDO}]_0:[M_{nBA}]_0:[Cu(I)Br]_0:[PMDETA]_0 = 1:50:50:1:1$, $T = 110$ °C.

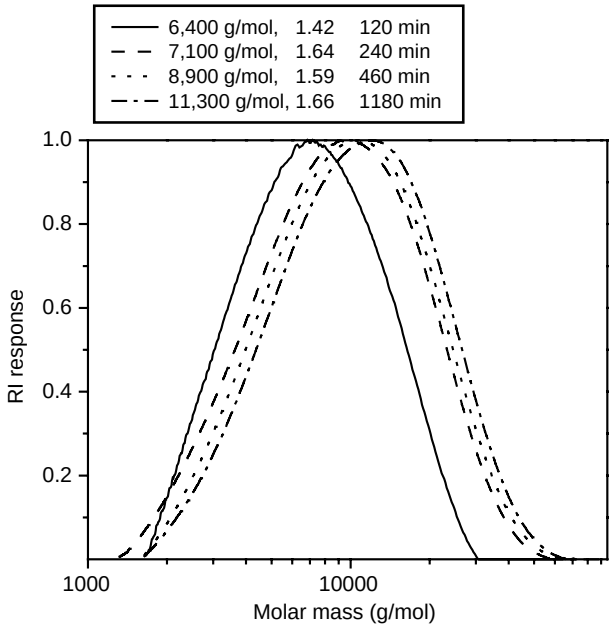



Fig. 2. GPC traces of copolymer samples taken during the copolymerization of BMDO with *n*BA (entry 4, Table 1). $[EBriBu]_0:[M]_0:[Cu(I)Br]_0:[PMDETA]_0 = 1:100:1:1$, $T = 110$ °C.

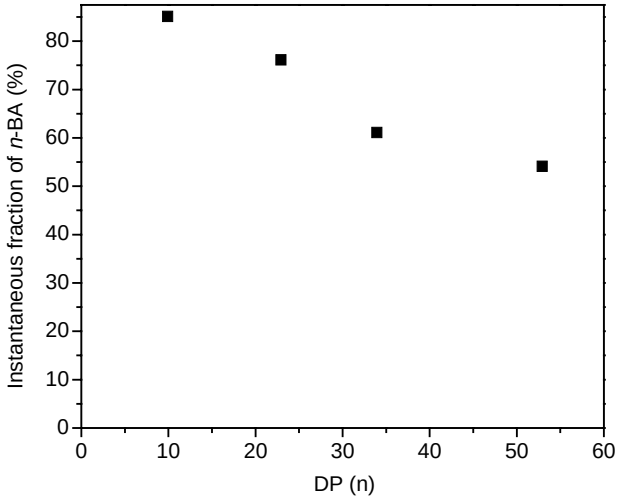



Fig. 3. The plot of instantaneous fraction of *n*BA vs. $DP_n$ for copolymerization of BMDO and *n*BA (entry 4, Table 1). $[EBriBu]_0:[M_{BMDO}]_0:[M_{nBA}]_0:[Cu(I)Br]_0:[PMDETA]_0 = 1:50:50:1:1$, $T = 110$ °C.

The general copolymerization behavior can be illustrated by a reaction where the initial feed ratio of comonomers was 50:50 (entry 4, Table 1). The plot of the first-order monomer consumption vs. time (Fig. 1) shows that *n*BA was consumed faster than BMDO in the copolymerization, indicating that *n*BA is more reactive than BMDO. The difference in their reactivities is attributed to their different molecular structures. BMDO is a vinyl acetal while *n*BA is an acrylate with a double bond conjugated with a carbonyl group. The downward trend of the first-order plot at the higher conversion could indicate that some termination occurred during the polymerization, leading to a decrease in the concentration of propagating polymeric radicals and consequently, the polymerization rate. Alternatively, rate could decrease due to equilibrium shifting towards less active growing species.

The GPC profiles show a progressive increase of the molecular weight during the polymerization (Fig. 2), demonstrating

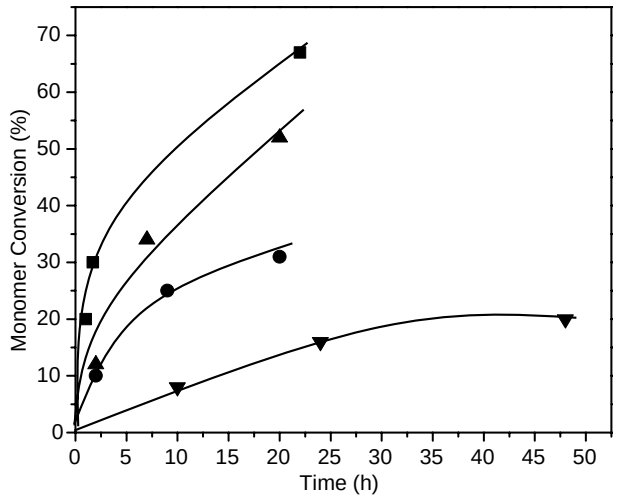



Fig. 4. The plot of total monomer conversion vs. time for copolymerization of BMDO with *n*BA at different feed ratios (BMDO mol%): 100 (▼), 80 (●), 50 (▲), 20 (■). $[EBriBu]_0:[M]_0:[Cu(I)Br]_0:[PMDETA]_0 = 1:100:1:1$, $T = 110$ °C.

Table 2
Calculation of monomer reactivity ratios

| Entries | $F = M_1/M_2$ | $f = m_1/m_2$ | $F^2/f$ | $\eta$ | $\xi$ |
|---|---|---|---|---|---|
| 1 | 4 | 0.65 | 24.6 | −0.07 | 0.83 |
| 2 | 0.25 | 0.064 | 0.98 | −0.62 | 0.17 |
| 3 | 1 | 0.25 | 4 | −0.34 | 0.45 |

$M_1$, mole fraction of BMDO in feed; $M_2$, mole fraction of *n*BA in feed, $m_1$, mole fraction of BMDO in copolymer; $m_2$, mole fraction of *n*BA in copolymer, $\alpha = \sqrt{(F^2/f)_{min}(F^2/f)_{max}}$, $\eta = ((F/f)(f-1))/(\alpha + (F^2/f))$, $\xi = (F^2/f)/(\alpha + (F^2/f))$.

relatively fast initiation and insignificant transfer. The relatively higher polydispersity (PDI) was probably due to the termination occurring in the copolymerization.

The plot of the instantaneous fraction of *n*BA in the copolymer with respect to the degree of polymerization (Fig. 3) shows a gradient in fraction of *n*BA in the polymer chain. These results indicate that at the early stage of polymerization, the BMDO radicals have a much greater tendency to react with a *n*BA monomer rather than another BMDO monomer, while *n*BA radicals also prefer to react with a *n*BA monomer. This leads to BMDO-*n*BA, *n*BA-BMDO and *n*BA-*n*BA sequences in the polymer chain with isolated BMDO units. As the polymerization progressed, the *n*BA concentration in the monomer mixture decreased and resulted in an increase in the instantaneous incorporation of BMDO. As a result, the possibility of formation of BMDO repetitive sequence in the polymer chain was enhanced. Therefore, the *n*BA-BMDO, BMDO-*n*BA, $(nBA)_n$, and $(BMDO)_n$ structures should coexist in the final copolymer product. This was verified using NMR spectroscopy described in the structural characterization section.

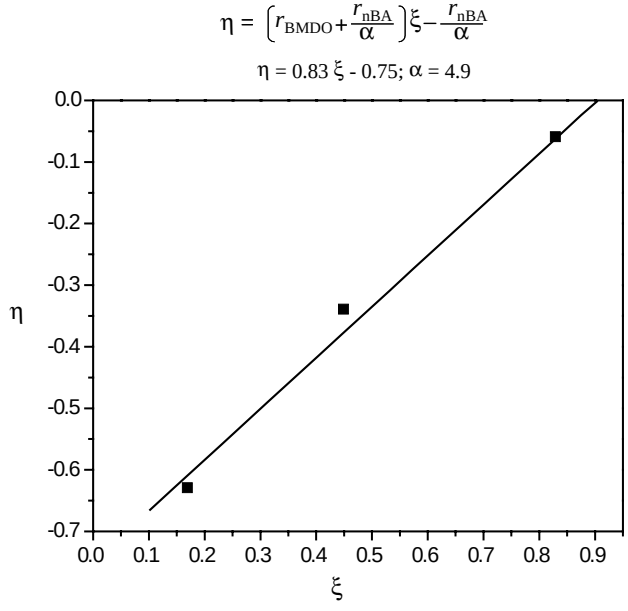



Fig. 5. Kelen–Tüdõs plot for copolymerization of BMDO with *n*BA. $F = M_{BMDO}/M_{nBA}$ (monomer feed ratio); $f = m_{BMDO}/m_{nBA}$ (copolymer composition); $\alpha = \sqrt{(F^2/f)_{min}(F^2/f)_{max}}$, $\eta = ((F/f)(f-1))/(\alpha + (F^2/f))$, $\xi = (F^2/f)/(\alpha + (F^2/f))$.

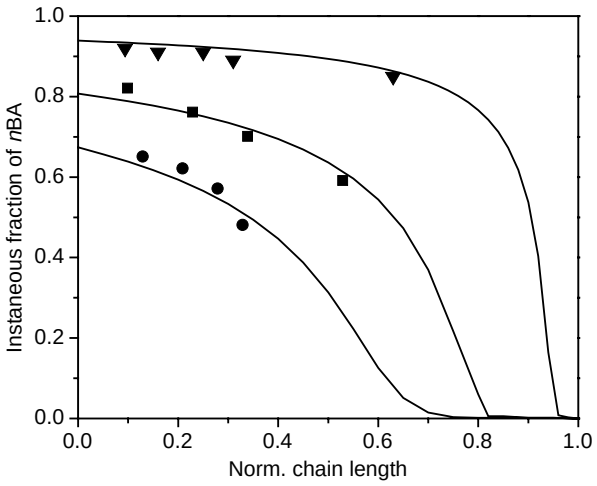
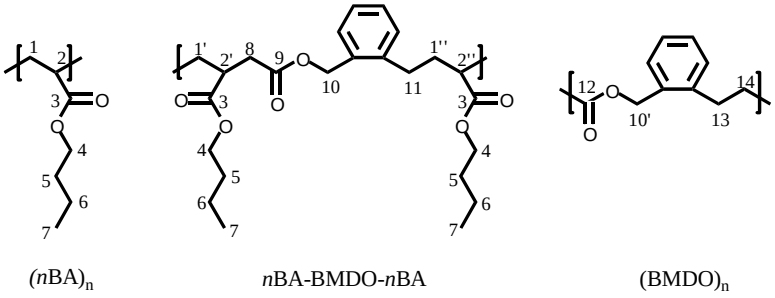



Fig. 6. Plots of instantaneous fraction of *n*BA vs. norm. chain length for copolymerization of BMDO and *n*BA at different monomer feed ratios. $[M_{BMDO}]_0$: $[M_{nBA}]_0 = 20{:}80$ (▼), $[M_{BMDO}]_0$: $[M_{nBA}]_0 = 50{:}50$ (■), $[M_{BMDO}]_0$: $[M_{nBA}]_0 = 70{:}30$ (●), theoretical prediction using $r_{BMDO} = 0.08$ and $r_{nBA} = 3.7$ (solid line). Normalized chain length = $DP_t/DP_{final}$; $DP_t$ = DP of the polymer obtained at different time intervals during the polymerization (based on $^1$H NMR); $DP_{final}$ = DP of the targeted polymer.

### 3.2. Variation in comonomer ratios

Various BMDO/*n*BA copolymers were synthesized by changing the molar ratio of these two monomers in the initial feed (Table 1). The effects of BMDO on the rate of the polymerization have been clearly observed. The polymerization rate decreased and lower monomer conversion was reached with increasing the amount of BMDO in the initial feed and (Fig. 4 and Table 1).

For each copolymerization at different monomer feed ratio (BMDO:*n*BA = 20:80, 50:50, 80:20), one copolymer sample was taken at low monomer conversion (<10%). The composition of those samples were determined by $^1$H NMR and used for calculating the monomer reactivity ratios according to the Kelen–Tüdõs method [21]. The calculation results and the notation descriptions are summarized in Table 2. The plot of $\eta$ vs. $\xi$ is shown in Fig. 5. From the slope and intercept of the linear best fit line, the monomer reactivity ratios of BMDO and *n*BA were determined to be $r_{BMDO} = 0.08$ and $r_{nBA} = 3.7$. Apparently, the values of monomer reactivity ratios indicate that growing radicals with *n*BA end were added to the *n*BA monomer with higher preference, while radicals with BMDO end also preferred to be added to the *n*BA monomer.



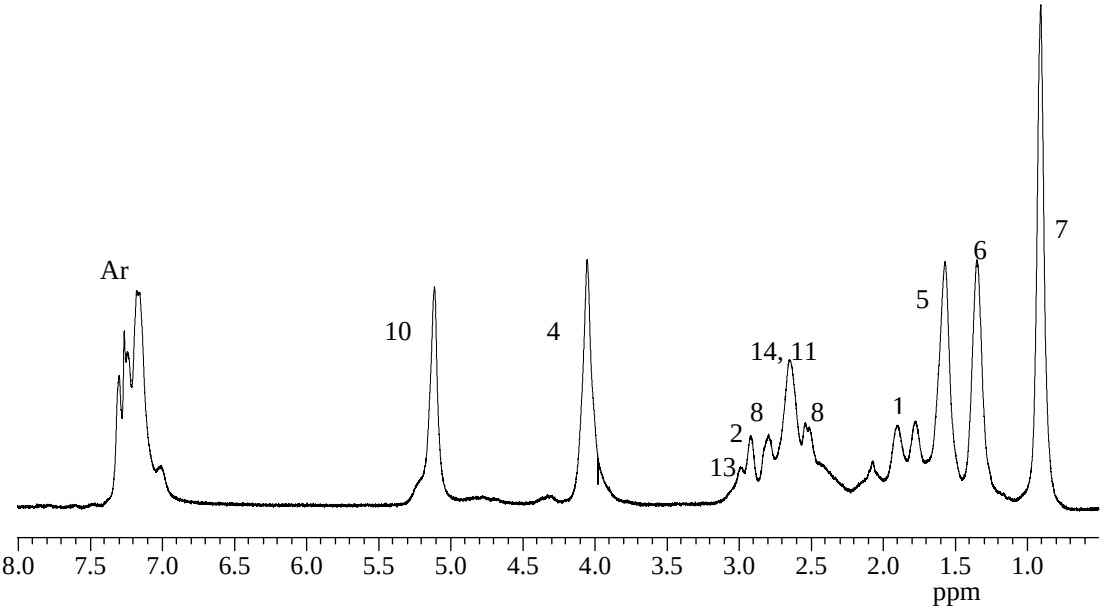
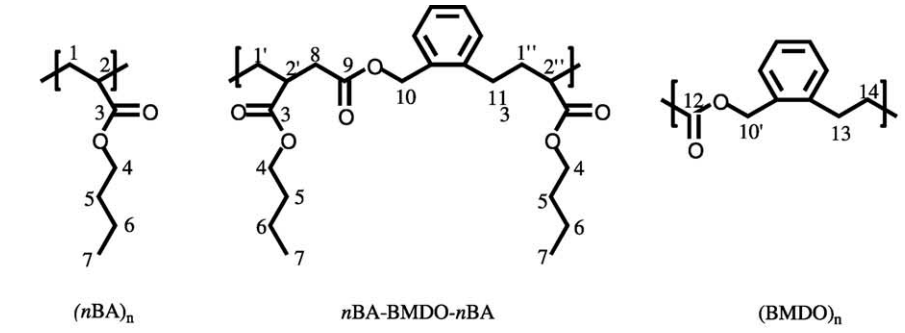




Fig. 7. $^1$H NMR spectrum of BMDO/*n*BA copolymer in $CDCl_3$ (entry 2, Table 1). $\delta_1 = \delta_{1'} = \delta_{1''}$, $\delta_2 = \delta_{2'} = \delta_{2''}$, $\delta_{10} = \delta_{10'}$.

The plots of the instantaneous fraction of *n*BA in the copolymer with respect to normalized chain length in polymerizations at different initial feed ratios of comonomers (Fig. 6) show a similar trend. The instantaneous incorporation of *n*BA into the copolymer chain decreased with progress of polymerization. All the contours of the obtained gradient copolymers followed the predicted drift simulated using the ProCop program [22] when assuming $r_{BMDO} = 0.08$ and $r_{nBA} = 3.7$. However, for the copolymerization at the initial feed ratio of BMDO:*n*BA = 20:80, the predicted sharp composition change varying from 0.9 to 0 was not observed in the experiment since high monomer conversion was not reached.

### 3.3. Structural characterization

The structural characterization of BMDO/*n*BA copolymers was performed using NMR spectroscopic techniques. The representative $^1$H NMR spectrum of one copolymer sample (BMDO:*n*BA = 80:20 (initial feed ratio), entry 2, Table 1) is shown in Fig. 7, where the characteristic proton signals of both *n*BA and BMDO units are present and marked. More information about the copolymer structure was obtained through 2D NMR spectroscopy techniques. The COSY experiment (not shown) led to unambiguous assignment of the spin system corresponding to the butyl side chain protons 4,



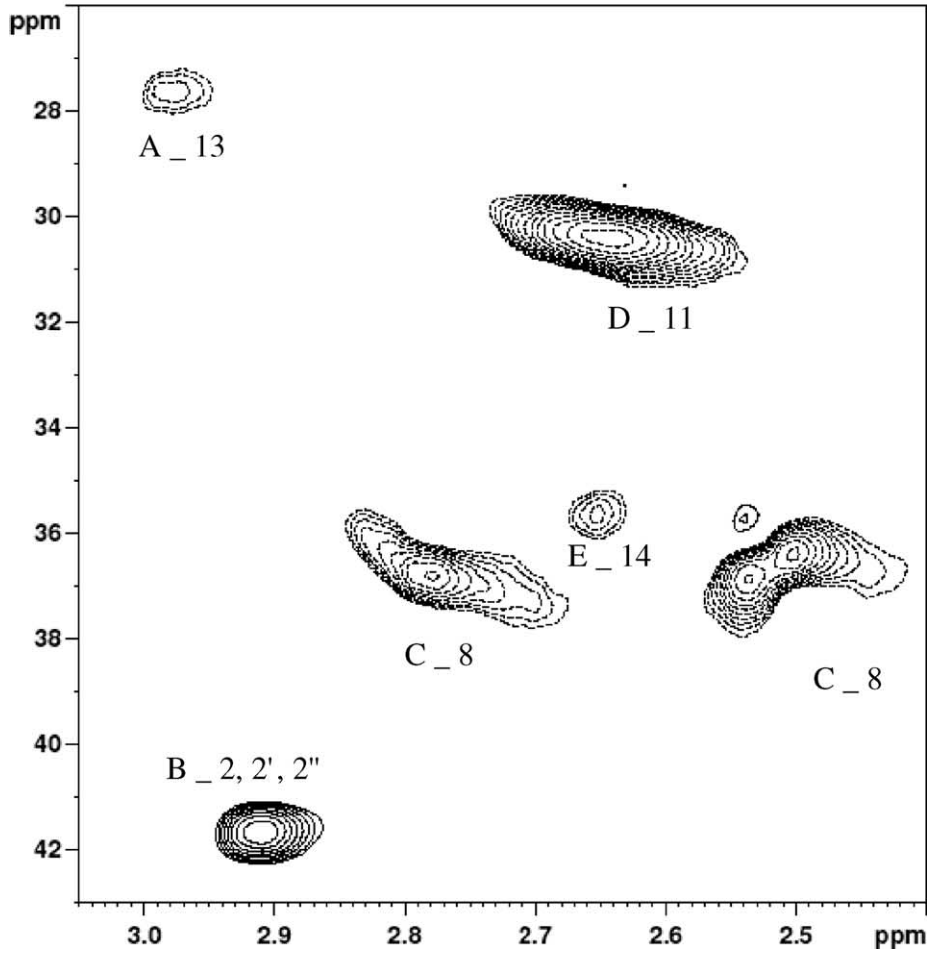




Fig. 8. Partially edited-$^1$H, $^{13}$C HSQC NMR spectrum of the BMDO/*n*BA copolymer in $CDCl_3$ (entry 2, Table 1). Cross peaks of $CH_2$ (dotted line), CH (solid line).

5, 6, and 7 of *n*BA unit. The edited-$^{1}$H, $^{13}$C HSQC provides not only one-bond proton-carbon correlations, but also information about the multiplicity of the carbon signal. Cross-peaks involving $CH_3$ and CH groups have positive phase (solid line), while cross-peaks from $CH_2$ groups have negative phase (dotted line). This is similar to having an HSQC and a DEPT-135 combined in a single experiment. The experiment (Fig. 8) showed a set of cross-peaks in the proton range of 2.4–3.1 ppm and the carbon range 26–43 ppm. The cross-peaks A, C, D and E showed negative phase ($CH_2$), while the cross-peak B showed positive phase (CH). The cross-peak A corresponds to the correlation of the proton at 2.98 ppm and carbon at 27.7 ppm, and was assigned to proton 13. Cross-peak B represents the correlation of protons 2, 2′, and 2″ at 2.92 ppm with their carbons at 41.7 ppm. Cross-peaks C are from the correlation of two nonequivalent protons 8 with their carbons at 36.5 ppm. The cross-peaks D and E are from the correlation of the protons at 2.65 ppm and carbons at 30.5 and 35.5 ppm, assigned to protons 11 and 14. Signals C are much stronger than A and E, indicating that BMDO units is preferentially surrounded by two *n*BA units.

The peak assignment was further confirmed by the 2D $^{1}$H–$^{13}$C HMBC spectrum (Fig. 9), which provides long-range (two- and three-bond) proton–carbon correlations. In Fig. 9(a) the cross-correlation peaks between proton 13 and three aromatic carbon signals at 129, 133, 137 ppm, one carbonyl carbon (12) at 173 ppm, and one methylene carbon (14) at 35.5 ppm were clearly observed. The correlation between protons 2, 2′, and 2″ with carbons at 35.7 (8), 33.7 (1,1′,1″), and 29.9 (11) ppm and two carbonyl carbons at 171 (9) and 175 ppm (3) was also observed, but it is very difficult to differentiate between them because the signals overlap.

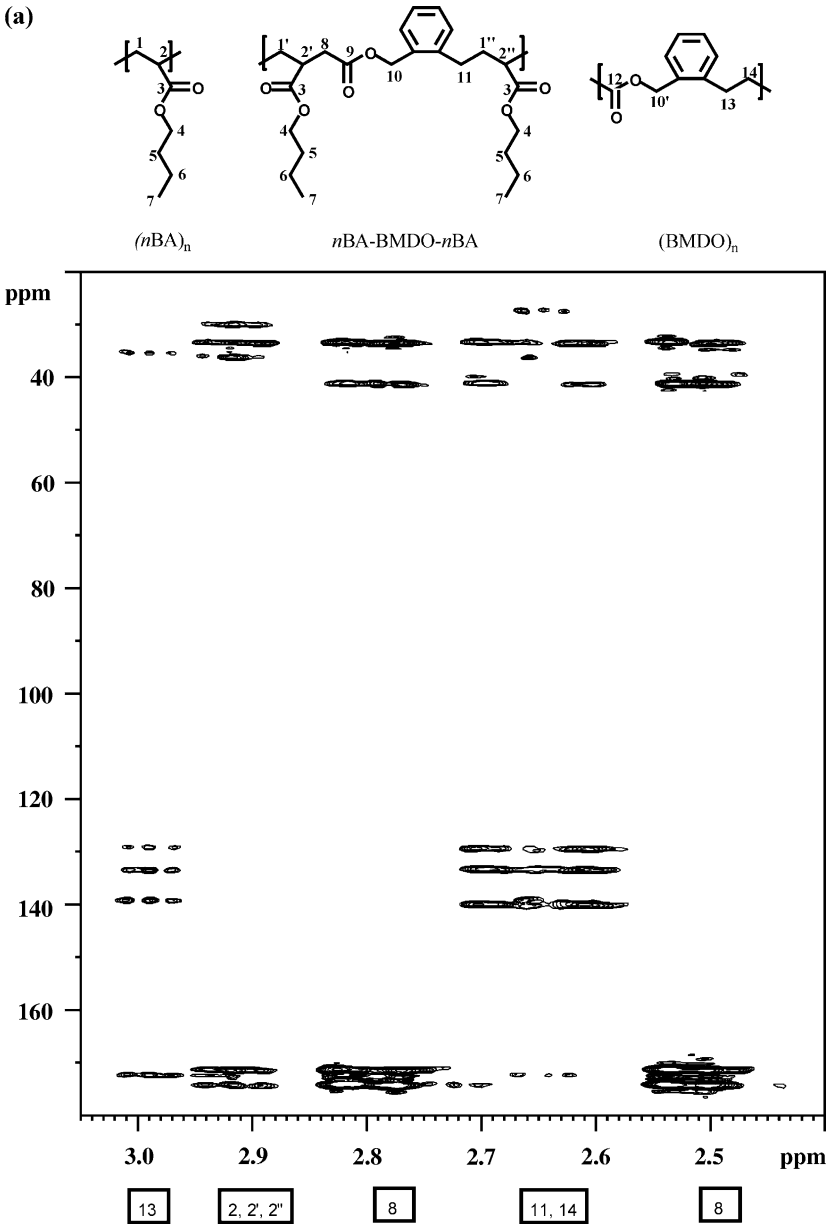



Fig. 9. Partial $^{1}$H–$^{13}$C HMBC NMR spectrum of the BMDO/*n*BA copolymer in $CDCl_3$: (a) 2.4–3.1 ppm; (b) 3.8–5.5 ppm (entry 2, Table 1).

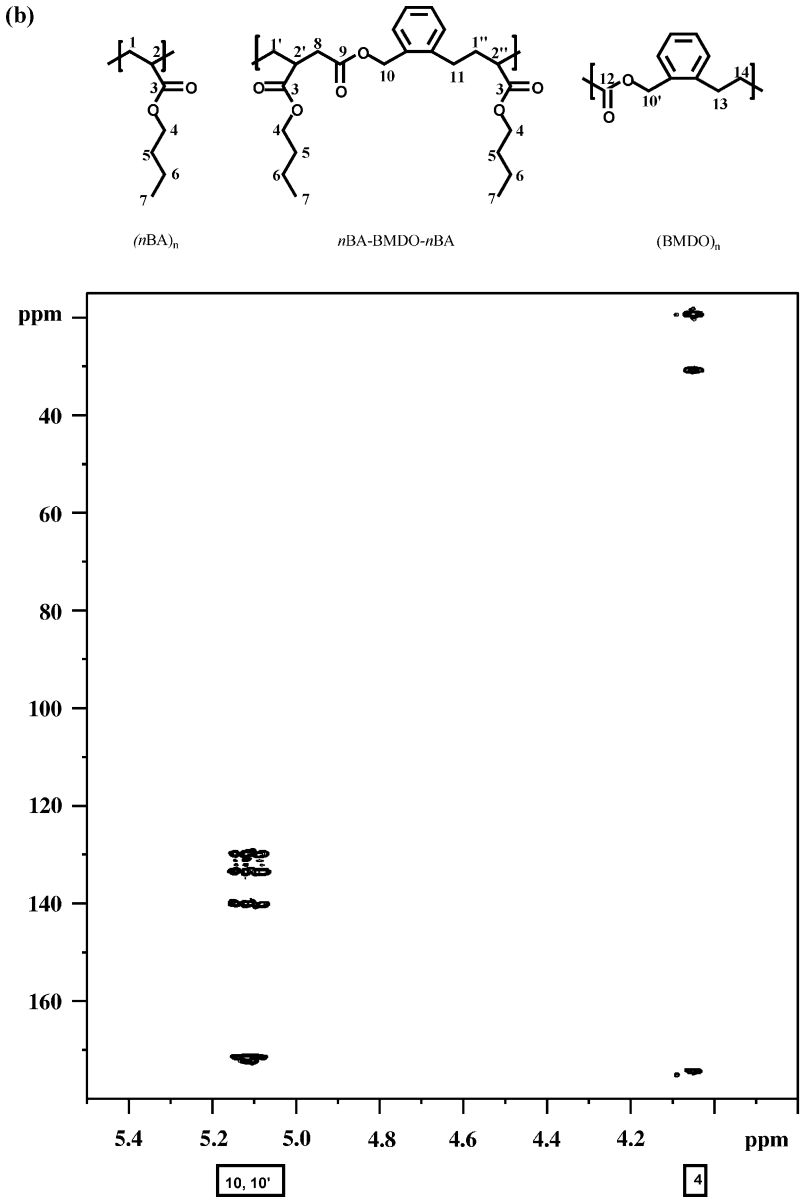



Fig. 9 (*continued*)

The protons centered at 2.5 and 2.8 ppm show no correlation with the aromatic carbons but do show correlation with two carbonyl groups, and were assigned to proton 8. The chemical shift of protons 11 and 14 are overlapping at the region around 2.65 ppm. The correlation with carbons at 27.1 ppm (13) and 173 ppm (12) indicates that the proton at the corresponding chemical shift was proton 14 from the BMDO segment. Other correlations at this region are from proton 11 with its corresponding carbons. Fig. 9(b) shows correlations of protons 10, 10′ at 5.1 ppm with three aromatic carbons and the carbonyl signal at 171 ppm, while proton 4 at 4.0 ppm shows correlations with two $CH_2$ carbon signals (5 and 6) and the carbonyl signal (3) from the butyl side chain at 175 ppm. These correlations permitted unambiguously differentiation between the carbon resonances of the carbonyl group in the side chains (175 pmm) from those of the main chain. The absence of signals between 100 and 110 ppm in the NMR spectra implies the absence of polyacetal linkages, indicating essentially quantitative ring opening of BMDO in this copolymerization.

### 3.4. Hydrolysis of BMDO/nBA copolymers

A study of the hydrolytic degradation was carried out under acidic condition. All BMDO/*n*BA copolymers were hydrolytically degradable, as revealed by a decrease in the molecular weight during hydrolysis. Degradation is illustrated in Fig. 10, showing the shift of GPC traces of the polymer samples during the hydrolysis of BMDO/*n*BA copolymer with 11 mol% BMDO (BDMO:*n*BA = 20:80 (initial feed ratio), entry 6, Table 1). After 0.5 h, the molecular weight of the copolymer decreased from $M_n$ = 20,500 g/mol to $M_n$ = 3100 g/mol. This demonstrates

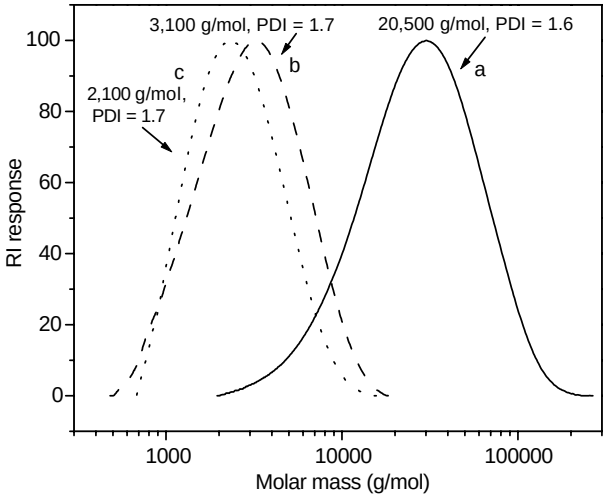



Fig. 10. GPC traces of BMDO/*n*BA copolymers (entry 6, Table 1) : (a) before hydrolysis; (b) after hydrolysis for 0.5 h; (c) after hydrolysis for 8 h. Copolymer: THF: 1-BuOH: $H_2SO_4$ = 50 mg: 3 mL: 2 mL: 2 drops, $T$ = 80 °C.

the successful introduction of hydrolytically degradable ester groups in the polymer main chain. With an increase of the hydrolysis time, the molecular weight of the copolymer continued decreasing and finally reached 2100 g/mol. The theoretical number average molecular weight of the final degraded product is expected to be 1400 g/mol for the copolymer at this composition ($M_{n,final} = M_{nBA} \times$ the amount of *n*BA units/the amount of BMDO units + $M_{BMDO} \times$ the amount of BMDO units). The amount of BMDO and *n*BA units in the copolymer was calculated based on the ratio of initiator to monomer and monomer conversion (not shown). Actual degraded product with higher molecular weight is probably due to the formation of some oligomers with low molecular weight, which cannot be detected by GPC.

## 4. Conclusions

The copolymerization of BMDO with *n*BA was successful under ATRP conditions. The reactivity ratios for the copolymerization of BMDO with *n*BA were determined using the Kelen–Tüdõs method and were found to be $r_{BMDO} = 0.08$ and $r_{nBA} = 3.7$. The quantitative ring opening of BMDO in the copolymerization was determined by 1D and 2D NMR spectroscopy techniques. The successful introduction of ester groups into the copolymer of BMDO/*n*BA by ring opening of BMDO was confirmed by hydrolytic degradation. Biodegradation studies of these copolymers are under way.

## Acknowledgements

Financial support from the industrial members of the CRP consortium at Carnegie Mellon University and NSF Grant Number CHE-04-05627 are greatly appreciated. Dr Brent Sumerlin, Daniel J. Siegwart, and Dr James Spanswick are acknowledged for helpful discussions.

## References

[1] Lu Y, Chen SC. Adv Drug Deliv Rev 2004;56:1621–33.
[2] Matthew HWT. In: Dumitriu S, editor. Polymeric biomaterials. 2nd ed. New York: Marcel Dekker; 2002. p. 167–86.
[3] Labhasetwar V, Chen B, Muller DWM, Bonadio J, Ciftci K, Muller K, et al. Adv Drug Deliv Rev 1997;24:109–20.
[4] Chu CC. In: Dumitriu S, editor. Polymeric biomaterials. 2nd ed. New York: Marcel Dekker; 2002. p. 491–544.
[5] Albertsson A-C, Varma IK. Adv Polym Sci 2002;157:1–40.
[6] Okada M. Prog Polym Sci 2001;27:87–133.
[7] (a) Sanda F, Endo T. J Polym Sci, Part A: Polym Chem 2000;39:265–76.
(b) Bailey WJ, Chou JL, Feng P-Z, Issari B, Kuruganti V, Zhou LL. J Macromol Sci Chem 1988;25:781–98.
(c) Bailey WJ, Chen PY, Chen SC, Chiao WB, Endo T, Gapud B, et al. Makromol Chem Macromol Symp 1986;6:81–100.
(d) Bailey WJ, Chen PY, Chen SC, Chiao WB, Endo T, Gapud B, et al. J Macromol Sci Chem 1984;A21:1611–39.
(e) Bailey WJ, Endo T. J Polym Sci, Polym Symp 1978;64:17–26.
[8] Takata T, Endo T. Expanding Monomers 1992;63–152.
[9] Jin S, Gonsalves KE. Macromolecules 1997;30:3104–6.
[10] Bailey WJ, Ni Z, Wu SR. Macromolecules 1982;15:711–4.
[11] Hiraguri Y, Tokiwa Y. J Polym Sci, Part A: Polym Chem 1993;31: 3159–61.
[12] (a) Rizzardo E, Chiefari J, Chong BYK, Ercole F, Krstina J, Jeffery J, et al. Macromol Symp 1999;143:291–307.
(b) Matyjaszewski K, Xia J. J Chem Rev 2001;101:2921–90.
(c) Kamigaito M, Ando T, Sawamoto M. Chem Rev 2001;101:3689–745.
(d) Hawker CJ, Bosman AW, Harth E. Chem Rev 2001;101:3661–88.
[13] (a) Wei Y, Connors EJ, Jia X, Wang B. Chem Mater 1996;8:604–6.
(b) Wei Y, Connors EJ, Jia X, Wang C. J Polym Sci, Part A: Polym Chem 1998;36:761–71.
[14] He T, Zou Y-F, Pan C-Y. Polym J (Tokyo, Japan) 2002;34:138–43.
[15] Yuan J-Y, Pan C-Y, Tang BZ. Macromolecules 2001;34:211–4.
[16] (a) Wickel H, Agarwal S. Macromolecules 2003;36:6152–9.
(b) Wickel H, Agarwal S, Greiner A. Macromolecules 2003;36: 2397–403.
[17] Chung IS, Matyjaszewski K. Macromolecules 2003;36:2995–8.
[18] Smith Q, Huang J, Matyjaszewski K, Loo Y-L. Macromolecules 2005;38: 5581–6.
[19] Grewe R, Struve A. Ber 1963;96:2819–21.
[20] (a) Xia J, Matyjaszewski K. Macromolecules 1997;30:7697–700.
(b) Huang J, Pintauer T, Matyjaszewski K. J Polym Sci, Part A: Polym Chem 2004;42:3285–92.
[21] Kelen T, Tudos F. J Macromol Sci Chem 1975;A9:1–27.
[22] Hagiopol C. Copolymerization—towards a systematic approach. New York: Kluwer-Academic/Plenum; 1999.