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Polymer 46 (2005) 10601–10606
polymer
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Controlled synthesis of poly(ε-caprolactone)-*graft*-polystyrene by atom transfer radical polymerization with poly(ε-caprolactone-*co*-α-bromo-ε-caprolactone) copolymer as macroinitiator

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Received 2 January 2005; received in revised form 5 June 2005; accepted 16 June 2005
Available online 21 September 2005

Abstract

A substituted ε-caprolactone, α-bromo-ε-caprolactone, was synthesized from α-bromocyclohexanone by Baeyer–Villiger reaction using 3-chloroperoxybenzoic acid. The ring-opening copolymerization of this monomer with ε-caprolactone was carried out with aluminum isopropoxide as the initiator, giving poly(ε-caprolactone-*co*-α-bromo-ε-caprolactone) copolymer. This copolymer was used as the macroinitiator for the controlled atom transfer radical polymerization (ATRP) of styrene for the synthesis of poly(ε-caprolactone)-*g*-polystyrene graft copolymers. The results showed that all the initiating sites along the macroinitiator chain initiated ATRP of styrene, and that the molecular weights of the graft copolymers increased with styrene conversion and agreed well with the theoretical values.

Keywords: Atom transfer radical polymerization (ATRP); Ring-opening polymerization; Graft copolymer

1. Introduction

Copolymers containing poly(ε-caprolactone) (PCL) blocks are interesting because they are miscible with a variety of polymers, including PVC, ABS, SAN, and PC [1]. A further interesting characteristic of PCL block is that its ester linkage undergoes exchange reactions with other polyesters, polyamides, and polycarbonates, etc. [2–4]. Generally, copolymers containing PCL blocks were prepared by ring-opening polymerization (ROP) of ε-caprolactone (CL) using a metallic catalyst derived from the hydroxyl-terminated polymers obtained by living ionic polymerization [5–11].

The last two decades have witnessed the emergence of new living polymerization techniques based on radical chemistry. Among them, stable free radical polymerization (SFRP) and atom transfer radical polymerization (ATRP) are the most successful methods which allow molecular weight, molecular weight distribution, and chain-end functionality to be controlled accurately [12–16]. These living radical polymerization methods have also been used in the preparation of block, graft, and star polymers containing PCL blocks. For example, Yoshida et al. prepared PCL with 2,2,6,6-tetramethylpiperidine-1-oxy (TEMPO) at one end through ROP of CL by an aluminum tri(4-oxy-TEMPO), and then used this PCL as a polymeric counter radical for SFRP of styrene, giving PCL-*b*-PSt in quantitative efficiency [17]. While Hsueh et al. reported a different way by using polystyrene containing a hydroxy chain end, which was obtained from SFRP of styrene in the presence of 4-hydroxy-TEMPO, as an initiator for ROP of CL [18]. Matyjaszewski et al. prepared SAN-*b*-PCL-*b*-SAN triblock copolymers using 2-bromoester of dihydroxy PCL as macroinitiator for copolymerization of styrene and acrylonitrile by copper-mediated ATRP [19]. Gagné synthesized PCL-*b*-PSt copolymer using α,ω-heterotelechelic PCL as a macroinitiator which was prepared by ring-opening/chain transfer protocol [20]. Hawker et al. [21,22] and Huang et al. [23] demonstrated that double-handed

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0032-3861/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2005.06.105

initiator can be used as a dual initiator for the living polymerization of dissimilar monomers without the need for intermediate activation or transformation steps. Hydroxy and alkoxyamine, or tribromo, initiating groups were found to be fully compatible with the reaction conditions for the living ROP of CL and nitroxide-mediated or atom transfer living radical polymerization. This permits well-defined block copolymers to be readily prepared in the minimum number reaction steps.

Recently, Hedrick et al. [24,25] reported the synthesis, polymerization, and copolymerization of a new substituted CL, γ-(2-bromo-2-methyl propionyl)-ε-caprolactone. The pendent 2-bromo-2-methyl propionyl groups were successfully used as macroinitiators for the ATRP of methyl methacrylate with the formation of PCL-*g*-poly(methyl methacrylate) graft copolymers. The sequential and concurrent polymerizations of γ-(2-bromo-2-methyl propionyl)-ε-caprolactone with 2-hydroxyethyl methacrylate generated branched copolymers [26].

In this paper, the synthesis of another substituted CL monomer, α-bromo-ε-caprolactone (αBrCL), will be reported. Moreover, the controlled synthesis of PCL-*g*-PSt by ATRP with poly(CL-*co*-αBrCL) copolymer as the macroinitiator will be presented.

2. Experimental

2.1. Materials

CL (Acros) was dried over calcium hydride for 48 h at room temperature and distilled under reduced pressure just before use. Toluene (Beijing Chemicals Plant) was dried by refluxing over calcium hydride for 4 h and distilled under reduced pressure. Cyclohexanone (Tianjin No. 2 Chemicals Plant) was distilled under nitrogen atmosphere. Styrene (Yanshan Petrochemical Co.) was dried over anhydrous $MgSO_4$, then distilled under reduced pressure and stored at −15 °C. Copper (I) bromide (CuBr) (Shanghai Zhenxing Chemical Regent Factory) was stirred in glacial acetic acid, filtered, and washed with acetone. The solid was dried under vacuum at room temperature overnight. 3-Chloroperoxybenzoic acid (75%) (Acros), aluminum isopropoxide (Tianjin Chemicals Research Institute), *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (Aldrich) and all other regents were used without any further purification.

2.2. Synthesis of α-bromocyclohexanone

It was synthesized by the slightly modified method of Kharasch et al. [27] and Allinger et al. [28]. To a stirred mixture of 30 g (0.306 mol) of cyclohexanone and 200 mL of distilled water, 49 g (0.306 mol) of bromine was added dropwise over a period of 5 h, during which the temperature was maintained between 25 and 30 °C by external cooling. When addition was completed, stirring was continued until the reaction mixture was colorless (about 1 h). The heavy organic layer was separated from the aqueous layer and dried over anhydrous $MgSO_4$. Pure α-bromocyclohexanone (37 g, 69% yield) was obtained by distillation.

2.3. Synthesis of αBrCL

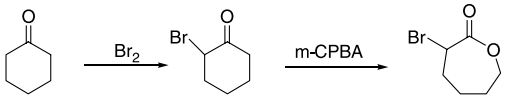
The procedure used was similar with that described for the preparation of α-chloro-ε-caprolactone [30]. Thirty-one grams of 3-chloroperoxybenzoic acid (0.135 mol) was added to a solution of 21.8 g (0.123 mol) of α-bromocyclohexanone in 200 mL of dichloromethane. After stirring at room temperature for 8 h, the reaction flask was placed in a refrigerator in order to precipitate 3-chlorobenzoic acid generated in the reaction. The solution was then filtered and washed with saturated solution of $Na_2S_2O_3$ three times, with a solution of $NaHCO_3$ three times, and finally with distilled water until neutral pH. The organic phase was dried with anhydrous $MgSO_4$ overnight. After $MgSO_4$ was filtered off, the solvent was removed by rotary evaporation. The crude product was dissolved in a mixture of hexane and ethyl acetate (10/3, volume ratio) and passed through a silica gel column prepared with the same solvent, collecting the second fraction. The solvent was removed by rotary evaporation, and the white solid was dried under vacuum overnight at room temperature. Yield: 12.5 g (53%). Melting point: 34.5 °C. Elemental analysis calculated for αBrCL: C, 37.33; H, 4.70. Found: C, 37.06; H, 4.79. ^{1}H NMR ($CDCl_3$, δ): 1.8–2.15 (m, 6H, –CH_2CH_2CH_2–), 4.3–4.7 (m, 2H, –COOCH_2–), 4.8 (m, –C*H*(Br)–) ppm. ^{13}C NMR ($CDCl_3$, δ): 169.8 (–*C*OO–), 69.8 (–*C*H(Br)–), 48.3 (–COO*C*H_2–), 31.8, 29.3, 25.3 (–*C*H_2*C*H_2*C*H_2–) ppm. IR: 2979, 2959, 2939, 2859, 1736, 1723, 1473, 1451, 1439, 1398, 1357, 1325, 1291, 1242, 1215, 1171, 1153, 1040, 986, 937, 857, 866, 830, 770, 738, 702, 571 cm^{-1}.

2.4. Copolymerization of CL and αBrCL via ROP

Copolymerization was carried out at 25 °C in toluene. To a 50 mL polymerization flask which was degassed by five vacuum-argon cycles, 15 mL of toluene, 0.628 g (3.25 mol) of αBrCL in toluene, 5.507 g (48.31 mmol) of CL, and 0.307 g of aluminum isopropoxide (1.5 mmol) in toluene were successively added through a rubber septum with a syringe. After polymerization for 3 h, an excess of 1 N HCl was added, and the copolymer was recovered by precipitation in cold methanol.

2.5. Grafting polymerization of styrene on poly(CL-co-αBrCL) copolymer via ATRP

Grafting polymerization was carried out as follows. 1.1478 g of poly(CL-*co*-αBrCL) copolymer obtained above and 0.082 g (0.57 mmol) of CuBr were charged into a 100 mL three-neck round-bottom flask equipped with



Scheme 1.

a stirring bar. After sealing it with rubber stopples, the flask was degassed and back-filled with argon five times and then left under argon. 0.1488 g (0.86 mmol) of *N*,*N*,*N′*,*N″*,*N″*-pentamethyldiethylenetriamine, 15.0 g of deoxygenated styrene and 30 mL of toluene were added to dissolve the macroinitiator. After the macroinitiator had been dissolved, the flask was immersed in an oil bath thermostated at 90 °C. At timed intervals, samples were withdrawn from the flask using degassed syringes to determine monomer conversion and molecular weight.

2.6. Characterization

Monomer conversion was obtained gravimetrically. Molecular weights and molecular weight distributions of macroinitiator and graft copolymers were measured using gel permeation chromatography (GPC), on a system equipped with a Waters 515 pump, three columns (Styragel HR1, Styragel HR3 and Styragel HT4) and a 2410 differential refractometer detector. The eluent was THF and the flow rate was 1 mL/min. Narrow polystyrene standards were used to generate the calibration curve. ^{1}H NMR spectra were obtained using a Bruker AC 400 NMR spectrometer. $CDCl_3$ was used as solvent.

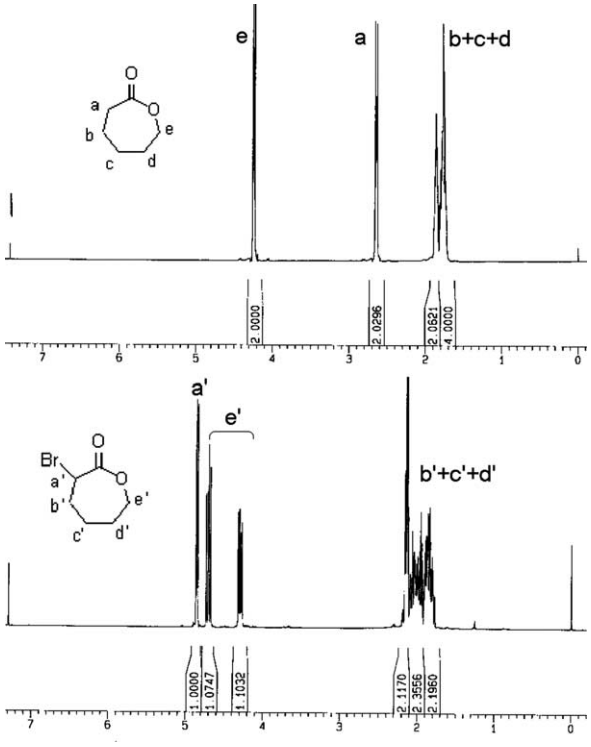


Fig. 1. ^{1}H NMR spectra of αBrCL (bottom) and CL (top) in $CDCl_3$.

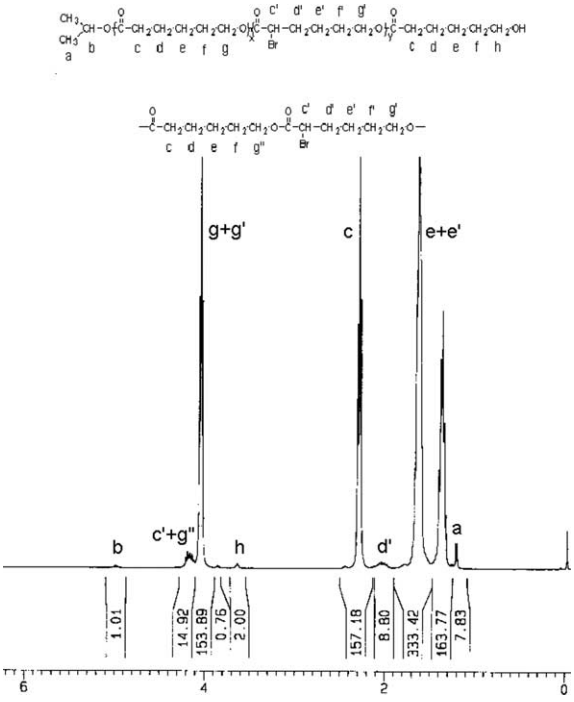


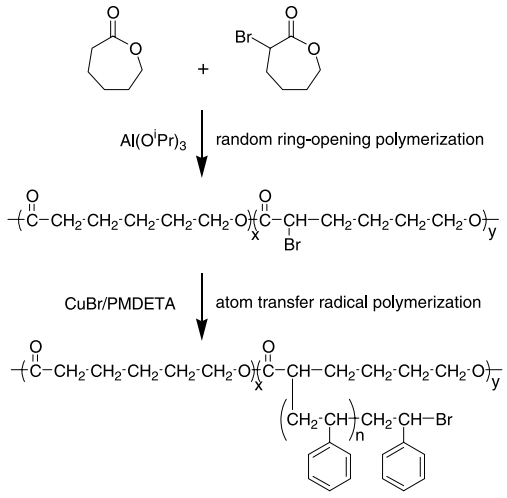
Fig. 2. ^{1}H NMR spectrum of poly(CL-*co*-αBrCL) copolymer in $CDCl_3$.

3. Results and discussion

3.1. Synthesis of αBrCL

Although αBrCL was ever used by Silks et al. [29] in the synthesis of 2-phenyltellurenyl-ε-caprolactone, they did not mentioned where it was bought from or how it was prepared. In this paper, αBrCL was synthesized as shown in Scheme 1.

Cyclohexanone was converted into α-bromocyclohexanone using bromine with 69% yield. The α-bromocyclohexanone was subsequently oxidized to αBrCL by the Baeyer–Villiger reaction using 3-chloroperoxybenzoic acid (mCPBA) with 53% yield. The ^{1}H NMR spectrum of αBrCL is shown in Fig. 1, and the spectrum is consistent with the assigned structure. For comparison, the ^{1}H NMR spectrum of CL is also shown in Fig. 1. It can be found that the proton at $\delta = 2.6$ ppm (H_a) had completely disappeared, and the multiplets at $\delta = 1.75$–1.87 ppm (H_b, H_c, H_d) and triplets at $\delta = 4.2$ ppm (H_e) had been shifted to higher fields ($\delta = 1.81$–2.16 ppm ($H_{b'}$, $H_{c'}$, $H_{d'}$), and 4.3–4.7 ppm ($H_{e'}$)), whereas correspondingly, new resonances at $\delta = 4.85$ ppm ($H_{a'}$) were observed.



Scheme 2.

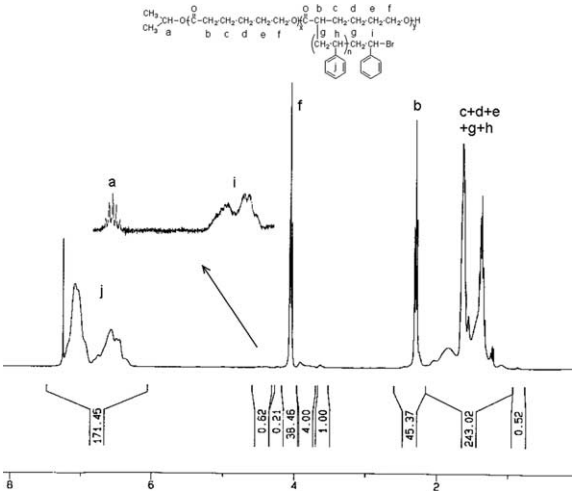


Fig. 4. ^{1}H NMR spectrum of PCL-*g*-PSt in $CDCl_3$ initiated by poly(CL-*co*-αBrCL) macroinitiator.

3.2. Syntheswis of macroinitiator poly(CL-co-αBrCL) by copolymerization of CL and αBrCL via ROP

Aluminum isopropoxide is a well-known efficient initiator in living ring-opening polymerization of CL, the mechanism of which involves the selective acyl-oxygen bond cleavage of the cyclic monomer. After the ultimate hydrolytic deactivation of the growing aluminum alkoxide species, the PCL chains are end-capped by a hydroxyl group and an isopropyl ester group, respectively [31].

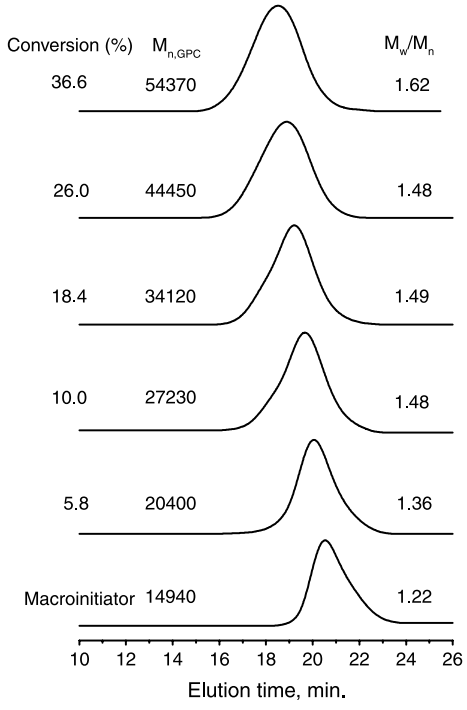


Fig. 3. GPC traces of graft copolymers obtained at different monomer conversions. (M_n obtained by GPC was calibrated with linear polystyrene standards).

Furthermore, structural similarities between αBrCL and CL might suggest that these two monomers polymerize according to the same mechanism. Therefore, the copolymerization of these two monomers was initiated by aluminum isopropoxide in toluene at 25 °C.

The ^{1}H NMR spectrum (Fig. 2) shows that the copolymer contains as many hydroxyl groups ($\delta = 3.75$ ppm, H_h) as isopropyl ester groups ($\delta = 5.0$ ppm, H_b). The molar fraction of the comonomers in the copolymer can be measured by ^{1}H NMR. Compared with the ^{1}H NMR spectrum of PCL, two new multiplets appear at $\delta = 4.10$–4.20 ppm ($H_{c'}$ of αBrCL monomeric unit and $H_{g''}$ of CL monomeric unit adjacent to αBrCL monomeric unit) and 1.95–2.05 ppm ($H_{d'}$ of αBrCL monomeric unit) in the ^{1}H NMR spectrum of the copolymer. With the area ratio of the peaks ($H_{d'}$ to $H_c + H_{d'}$), the molar fraction of αBrCL ($F_{\alpha BrCL}$) in the copolymer was 0.053, which was somewhat lower than that of αBrCL in the comonomer feed ($F_{\alpha BrCL} = 0.063$). According to the relative intensity of the isopropyl end group from the initiator and the methylene protons of the monomeric units, and taking account of the molar fraction of the comonomers in the copolymer, the number average molecular weight of the copolymer was calculated to be 9960. Furthermore, there were 4.4 αBrCL monomeric units per copolymer chain in average from the ratio of H_b to $H_{d'}$.

3.3. Synthesis of PCL-g-PSt graft copolymers by ATRP with poly(CL-co-αBrCL) as macroinitiator

The chemical environment of the bromide atom on the polyester chain is the same as that in alkyl 2-bromopropionate, which has be used as an effective initiator for ATRP of acrylate and styrene [12]. Therefore, poly(CL-*co*-αBrCL) copolymer was used as the macroinitiator for the preparation of the graft copolymers (Scheme 2).

Table 1
Characteristics of graft copolymers

Reaction time (h)	Conv. (wt%)	M_n Theoretical[a]	M_n NMR	M_n GPC	M_w/M_n
Macroinitiator			9960	14,940	1.22
1.33	5.8	16,780	16,540	20,400	1.36
3	10	21,830	23,340	27,230	1.48
5	18.4	32,390	32,490	34,120	1.49
9	26	41,780	41,560	44,450	1.48
16	36.6	54,940	52,290	58,370	1.53

[a] $M_{n,th} = M_n$ of the macroinitiator + weight of styrene polymerized (g)/amount of macroinitiator added (mmol).

Fig. 3 shows the resulting GPC traces of graft copolymers obtained at different monomer conversions. As conversion of styrene increased, the molecular weight distributions of the graft copolymers were unimodal and clearly shifted to higher molecular weights without any contamination of the unreacted macroinitiator.

^{1}H NMR spectrum of one of the graft copolymers is shown in Fig. 4. The real number average molecular weight of the graft copolymer could be calculated using the following equation from that of macroinitiator, and the integration of representative signal for styrene monomeric unit at 6.5–7.2 ppm and that for CL monomeric unit at 4.0 ppm.

$$M_{n,\,NMR} = M_{n,\,macroinitiator} + \frac{(I_j \times 104)/5}{(I_f \times 114)/2} M_{n,\,macroinitiator}$$

Here, I_j, I_f, 104, 114 and $M_{n,macroinitiator}$ are the integral values of peaks at 6.5–7.2 and 4.0 ppm, molecular weight of styrene, CL and macroinitiator, respectively.

The number average molecular weight from ^{1}H NMR increased in direct proportion to monomer conversion and agreed well with the theoretical values (Table 1).

In addition to the large absorptions of the repeated units for styrene and caprolactone, there appeared a new signal at 4.4 ppm in the ^{1}H NMR spectrum of the graft copolymer. It can be ascribed to the methine proton of styrene monomeric unit adjacent to the ω-end bromide. At the same time, the signal at 4.1–4.2 ppm disappeared. The observed peak intensity ratio of the methine proton of isopropyl ester group of the macroinitiator to the methine proton of styrene monomeric unit adjacent to the ω-end bromide was 5.0, which was close to the number (4.4) of BrCL monomeric units per macroinitiator chain reported above. This shows that all initiating sites along the macroinitiator chain initiated the ATRP of styrene.

To further confirm the graft copolymer structure, the graft copolymer listed in Table 1 with 36.6% conversion was hydrolyzed using KOH in a mixture of THF and ethanol. The polystyrene graft chain was recovered by precipitation in a large excess of methanol. Analysis of the product by ^{1}H NMR clearly shows the disappearance of the resonances due to the backbone. Its number average molecular weight and molecular weight distribution determined by GPC calibrated with narrow polystyrene standards was 11,230 and 1.24, respectively. The molecular weight by GPC was also agreed well with the calculated value (10,100) assuming that one living polystyrene graft chain forms from one initiating site.

4. Conclusion

In conclusion, poly(CL-*co*-αBrCL) copolymer can be used as the macroinitiator for ATRP of styrene, resulting PC-*g*-PSt graft copolymers. All initiating sites along the macroinitiator chain can initiate ATRP of styrene. The molecular weights of the graft copolymers increased with styrene conversion and agreed well with the theoretical values.

References

[1] Olabisi O, Robeson LE, Shaw MT. Polymer polymer miscibility. New York: Academic; 1979.
[2] Denchev Z, Bojkova A, Duchesne A, Stamm M, Fakirov S, Keul H, et al. Macromol Chem Phys 1998;199:2153–64.
[3] Kricheldorf H, Kreiser I. J Macromol Sci, Chem 1987;A24:1345–56.
[4] Jonza JM, Porter RS. Macromolecules 1986;19:1946–51.
[5] Heuschen J, Jérôme R, Teyssié P. Macromolecules 1981;14:242–6.
[6] Gervais M, Gallot B, Jérôme R, Teyssié P. Makromol Chem 1981; 182:989–95.
[7] Herman JJ, Jérôme R, Teyssié P, Gervais M, Gallot B. Makromol Chem 1981;182:997–1008.
[8] Heuschen J, Jérôme R, Teyssié P. J Polym Sci, Part B: Polym Phys 1989;27:523–44.
[9] Gorda KR, Peiffer DC, Chung TC, Berluche E. Polym Commun 1990; 31:286–9.
[10] Balsamo V, von Gyldefeldt F, Stadler R. Macromol Chem Phys 1996; 197:1159–69.
[11] Pilati F, Toselli M, Messori M, Priola A, Bongiovanni R, Malucelli G, et al. Macromolecules 1999;32:6969–76.
[12] Matyjaszewski K, Xia J. Chem Rev 2001;101:2921–90.
[13] Kamigaito M, Ando T, Sawamoto M. Chem Rev 2001;101:3689–745.
[14] Malmström EE, Hawker CJ. Macromol Chem Phys 1998;199:923–35.
[15] Colombani D. Prog Polym Sci 1997;22:1649–720.
[16] Georges MK, Veregin RPN, Kazmaier PM, Hamer GK. Macromolecules 1993;26:2987–9.
[17] Yoshida E, Osagawa Y. Macromolecules 1998;31:1446–53.
[18] Hsueh ML, Huang BH, Lin CC. Macromolecules 2002;35:5763–8.
[19] Tsarevsky NV, Sarbu T, Göbelt B, Matyjaszewski K. Macromolecules 2002;35:6142–8.
[20] Korn MR, Lennon JD, Glish GL, Gagné MR. Macromolecules 1999; 32:5149–53.

[21] Hawker CJ, Hedrick JL, Malmström EE, Trollsås M, Mecerryes D, Moineau G, et al. Macromolecules 1998;31:213–9.
[22] Mecerryes D, Moineau G, Dubois P, Jérôme R, Hedrick JL, Hawker C J, et al. Angew Chem Int Ed 1998;37:1274–6.
[23] Huang CF, Kuo SW, Lee HF, Chang FC. Polymer 2005;46:1561–5.
[24] Mecerreyes D, Atthoff B, Boduch KA, Trollsås M, Hedrick JL. Macromolecules 1999;32:5175–82.
[25] Detrebleur C, Mazza M, Lou X, Halleux O, Lecomte P, Mecerreyes D, et al. Macromolecules 2000;33:7751–60.
[26] Mecerryes D, Trollsås M, Hedrick JL. Macromolecules 1999;32: 8753–9.
[27] Kharasch MS, Sosnovsky G. J Org Chem 1958;23:1322–6.
[28] Allinger J, Allinger NL. Tetrahedron 1958;2:64–74.
[29] Luo X, Detrembleur C, Lecomte P, Jérôme R. J Polym Sci, Part A: Polym Chem 2002;40:2286–97.
[30] Silks LA, Odom JD, Dunlap RB. Synth Commun 1991;21:1105–19.
[31] Löfgren A, Albertsson AC, Dubois P, Jérôme R. J Macromol Sci, Rev Macromol Chem Phys 1995;C35:379–418.