Polymer Bulletin 46, 363–369 (2001)

Polymer Bulletin

Molecular-weight-controlled polymerization of styrene with $Mn(acac)_3$ in combination with organic halides

Kiyoshi Endo (✉), Akitoshi Yachi

Department of Applied Chemistry, Faculty of Engineering, Osaka City University, Sugimoto,
Sumiyoshi-ku, Osaka 558-8585, Japan
e-mail: endo@a-chem.eng.osaka-cu.ac.jp, Fax: +81-6-6605-2697

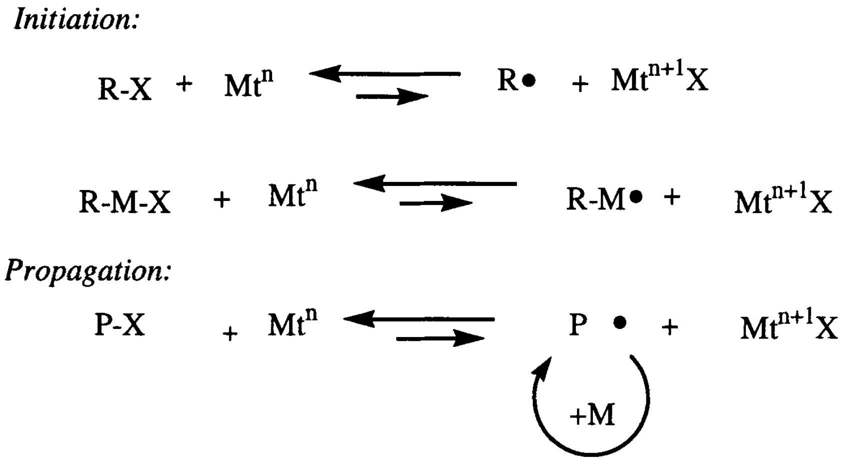
Received: 18 December 2000/Revised version: 19 April 2001/Accepted: 25 April 2001

Summary

The control of molecular weight of polymers in polymerization of styrene (St) with manganese(III) acetylacetonate [$Mn(acac)_3$] in the presence of organic halides (RX) in toluene at 80°C was investigated. In the polymerizations of St with $Mn(acac)_3$ in combination with benzyl bromide (BzBr) as RX, the molecular weight of the polymer increased with polymer yields, and the relationships between the molecular weight of polymer and polymer yield gave a straight line passing through the original point. However, the molecular weight distribution was not narrow, but kept almost constant (M_w/M_n was about 2) throughout the polymerization. The mechanism of the polymerization of St with $Mn(acac)_3$-BzBr was also discussed.

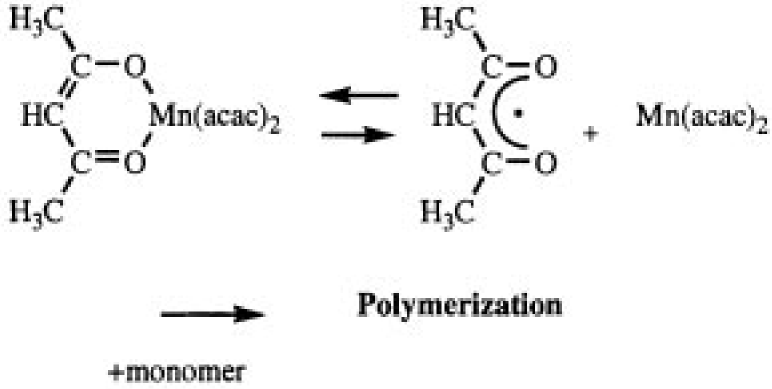
Introduction

Living radical polymerization is fascinating method from the view point of macromolecular architecture □ and now has well developed [1]. This polymerization can control the molecular weight and the molecular weight distribution of the polymers, since chain transfer reactions and a termination reaction by bimolecular propagating radicals were neglected. The bond formed at the chain end during the polymerization is able to cleave again by physical or chemical stimulus to yield the propagating radicals and stable radicals. The living radical polymerization was achieved by nitoroxides mediated polymerization using 2,2,6,6-tetramethyl-4-piperidinyloxy (TEMPO), transition-metals-mediated radical polymerization [2,3], a reversible addition fragmentation chain transfer (RAFT) process [5], and iniferter [6] process. Among them, the living radical polymerization with transition metal compound [Mt] in combination with organic halides (RX) has the advantage of applying for various vinyl monomers under mild conditions such as relatively low temperature like 60°C. The mechanism for the living radical polymerization with Mt/RX was proposed as shown in Scheme 1. In this polymerization system, Ru [2], Cu [3], Fe [10], Ni [7], Rh [8], and Pd [9] complexes were used as the transition metals. When RX used has a similar structure to that of the monomer used, the rate of initiation becomes faster with comparable rate of the propagation [4]. The effect of additive such as aluminum isopropoxide ($Al(O\textit{i}Pr)_3$) and 2,2'-bipyridine (bpy) was reported. From the proposed polymerization mechanism, other transition metal complexes are also expected to induce the living radical polymerization.



Scheme 1 Polymerization mechanism of ATRP (Mt : transition metal, M : monomer)

Transition metal acetylacetonate [Mt(acac)$_x$] was reported to initiate radical polymerizations of vinyl monomers [11,12]. Among Mt(acac)x investigated, Mn(acac)$_3$ revealed a high activity for the polymerization of St and methyl methacrylate (MMA). The proposed mechanism for the polymerization with Mn(acac)$_3$ alone is shown in Scheme 2 [11]. Taking the polymerization mechanism into consideration, Mt(acac)$_x$ in combination with RX system seems to be effective for the polymerization of various vinyl monomers. Nevertheless, polymerization of vinyl monomers with Mn(acac)$_3$ in the presence of RX has not been investigated. If the polymerization proceeds with Mn(acac)$_3$-RX by a similar mechanism with the transition metals mediated radical polymerization, it will be possible to control the molecular weight of the polymers. We reports here the polymerization of St with the Mn(acac)$_3$-RX.



Scheme 2 The proposed mechanism for the polymerization with Mn(acac)$_3$

Experimental

Materials

Commercially available Mt(acac)x were used as received. St, benzyl bromide (BzBr) and methyl 2-bromopropionate (MBP) were distilled over calcium hydride before use. Solvents and other reagents were purified by conventional methods.

Polymerization Procedure

Polymerization was carried out in sealed glass tube in a thermostat at 80°C for a given time. After the required amounts of reagents were charged, the tube was degassed and then sealed under high vacuum. After the polymerization, the tube was opened, and the contents of the tube were poured into a large amount of methanol to precipitate the polymer formed. The polymers were washed well with an excess of methanol, and dried in *vacuo* at room temperature. The polymer yield was determined by gravimetry.

Characterization

The number average (M_n) and weight average (M_w) molecular weight of the polymers were determined by GPC using a Tosoh GPC-8800 at 38°C in THF as calibrated with poly(St) standards. The ^{1}H NMR spectra for the polymers were recorded on JEOL JMN A-400 spectrometer in $CDCl_3$ at 50°C. The IR spectra of the polymers were recorded on JEOL FT-IR 430 spectrometer.

Results and discussion

Polymerization of St with Mn(acac)$_3$-BzBr

Polymerization of St with transition metal acetylacetonate [Mt(acac)$_x$] in combination with BzBr were conducted, and the results are listed in Table1. Some Mt(acac)$_x$ in the presence of BzBr were found to initiate the polymerization of St giving high molecular weight polymers. Although Mn(acac)$_3$-BzBr showed a high activity for the polymerization of St among Mt(acac)$_x$ examined, the Mn(acac)$_2$-BzBr afforded the polymer in a low yield. This seems to be a difference in initiation ability.

The effect of BzBr on the polymerization of St with Mn(acac)$_3$-RX was examined. The results are shown in Figure 1, in which the polymerization of St in the absence of BzBr is also indicated for comparison. In the polymerization of St with Mn(acac)$_3$ alone, the polymer yield increased with reaction time at the initial stage of the polymerization, but soon after the polymerization hardly proceeded. On the contrary, in the polymerization of St with Mn(acac)$_3$-BzBr, the polymer yield increased as a function of reaction time. The relationship between M_n of the polymers and polymer yield gave a straight line, and it passed through the original point as shown in Figure 2. Although the M_w/M_n of the polymer was about 2, the values kept constant throughout the polymerization. The GPC elution curves for the polymers obtained with Mn(acac)$_3$- BzBr shifted to the higher molecular weight side with reaction time as shown in Figure 3. Accordingly, it is clear that the molecular weight of the polymers is able to be controlled in the polymerization of St with Mn(acac)$_3$- BzBr.

Table1 Polymerization of St with $Mt(acac)_x$-BzBr in toluene at 80 °C for 24h.

$Mt(acac)_x$	Yield(%)	$M_n \times 10^{-5}$	M_w / M_n
$Mn(acac)_3$	63.4	1.9	2.32
$Mn(acac)_2$	7.0	3.3	2.58
$Fe(acac)_3$	3.5	1.5	1.75
$Co(acac)_3$	15.6	1.8	1.63
$Ni(acac)_2$	11.2	3.1	1.82
$Cu(acac)_2$	26.1	4.1	1.87

$[Mt(acac)_x] = 2.0 \times 10^{-3}$ mol/l, $[BzBr] = 4.0 \times 10^{-3}$ mol/l, $[St] = 5.4$ mol/l.

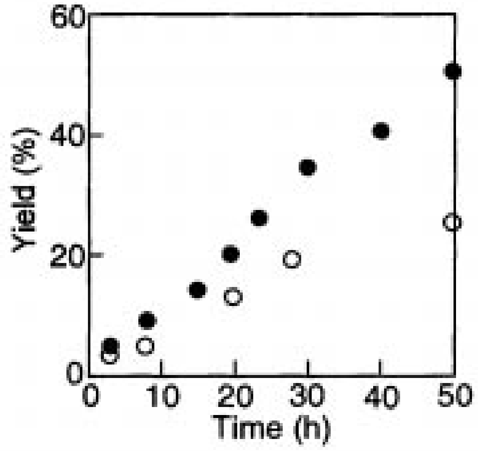


Fig. 1 Polymerization of St with $Mn(acac)_3$ (○) and $Mn(acac)_3$-BzBr (●)

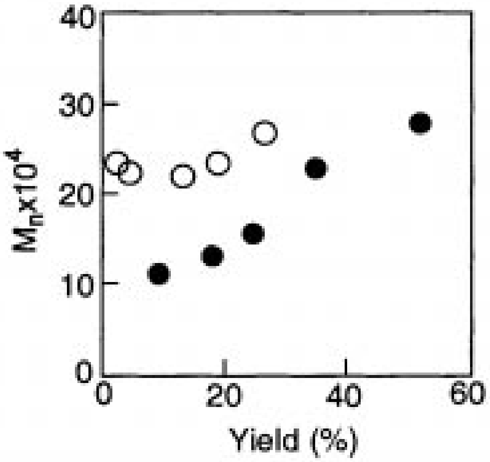


Fig. 2 Polymerization of St with $Mn(acac)_3$ (○), $Mn(acac)_3$-BzBr (●)

Polymerization Mechanism

To elucidate the mechanism for polymerization of St with $Mn(acac)_3$-RX, the copolymerization [13] of St (M_1) and MMA (M_2) with $Mn(acac)_3$-BzBr was investigated. The monomer reactivity ratios were determined to be $r_1 = 0.52$, $r_2 = 0.46$, which are in good agreement with those obtained from radical copolymerization initiated by AIBN ($r_1 = 0.52$, $r_2 = 0.32$) [14]. The triad tacticity of the poly(St) was determined to be mm=10%, mr=24%, and rr=66%, which agrees well with that obtained with AIBN (mm=14%, mr=30%, rr=56%) [15]. Thus, it is clear that the polymerization of St and MMA with the $Mn(acac)_3$-BzBr proceeds *via* a radical intermediate.

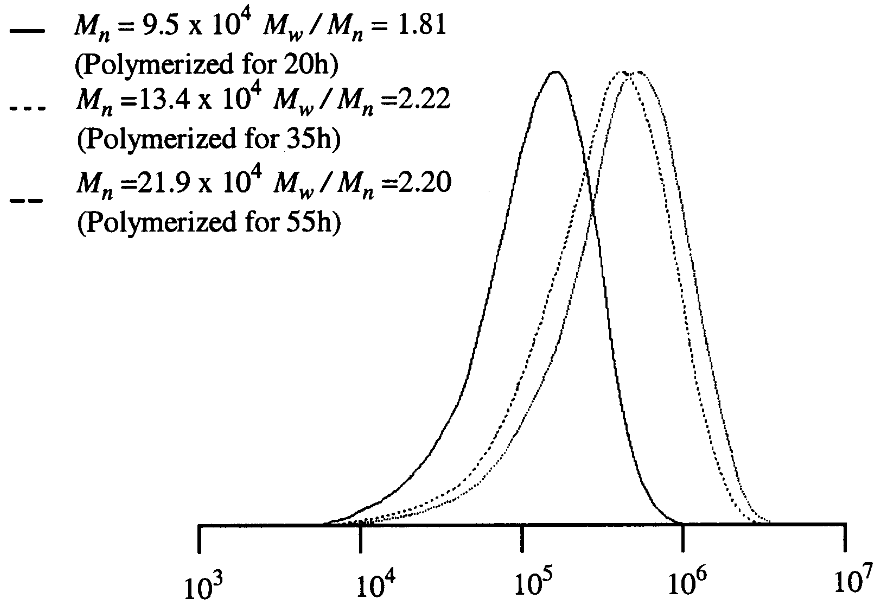


Fig. 3 GPC elution curves for the polymer obtained with $Mn(acac)_3$ – BzBr

The structure of the polymer obtained from the polymerization of St with $Mn(acac)_3$-BzBr was determined by NMR spectroscopy. When the BzBr was used , the polymer chain end could not be determined by an overlapping of the signal based on the St unit. So we used MBP instead of BzBr as a RX, and the polymerization of St with $Mn(acac)_3$-MBP was performed. The relationship between polymer yield and molecular weight was also linear through the original point. The ^{1}H NMR spectrum of the formed polymer is shown in Figure 4, in which signals based on the methyl proton peak at the initiation end derived from MPB were observed at 0.8 ppm, along with the peaks based on the main chain of the St units [16]. In addition, a signal attributed to the methine proton adjacent to the bromine atom was observed at 4.9 ppm, which was

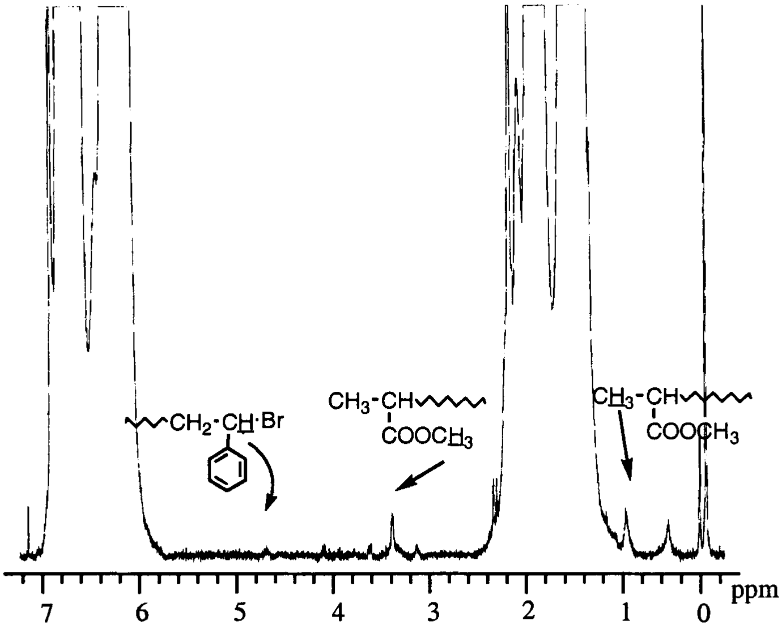
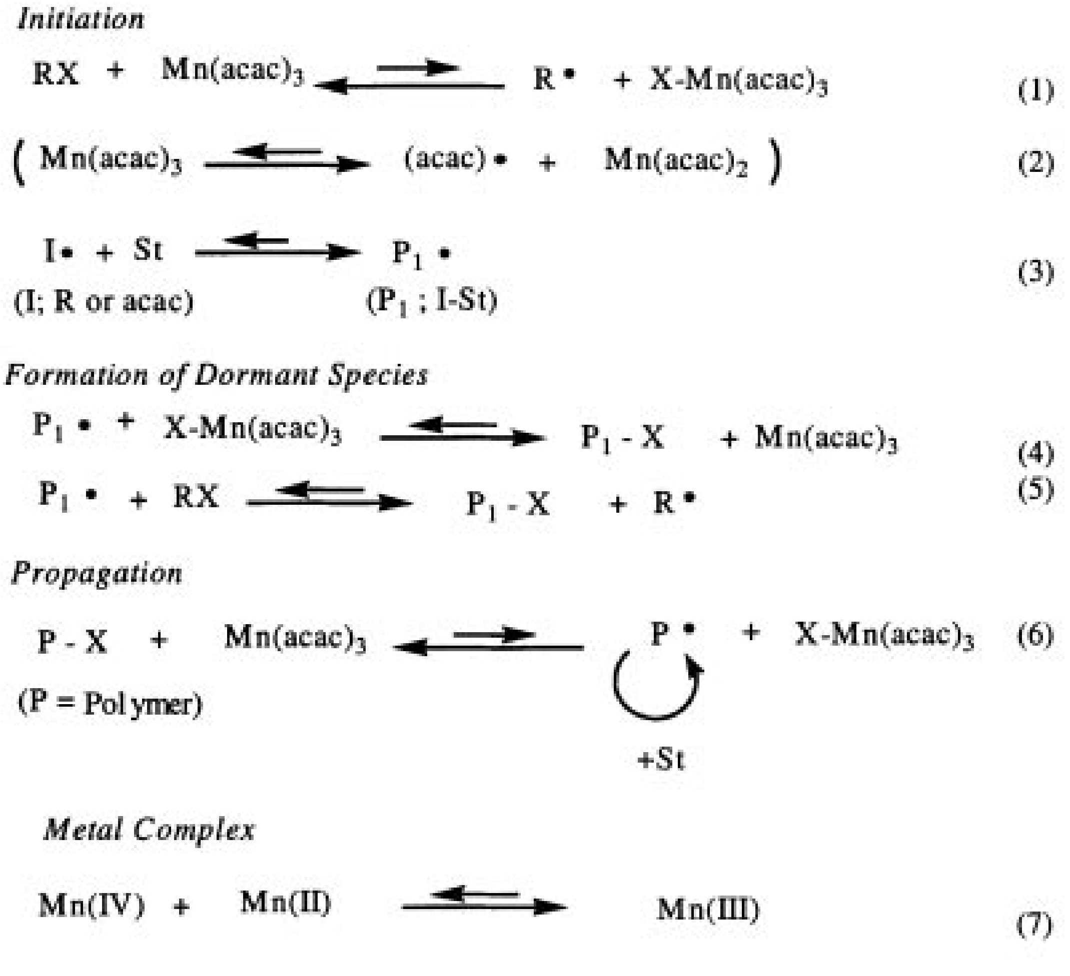


Fig. 4 ^{1}H-NMR spectrum of the poly(St) obtained with $Mn(acac)_3$ – MBP

assigned as the terminal chain end. This indicates that BzBr as well as MBP acts as an initiator for the polymerization of St, and the BzBr plays an important role to control the molecular weight of the resulting polymers.

The IR spectra of the polymer obtained from the polymerization with the Mn(acac)$_3$-BzBr showed a characteristic absorption at 1720cm^{-1} based on the carbonyl group derived from the ligand of Mn(acac)$_3$. The activity of Mn(acac)$_2$-BzBr for the polymerization of St was low. From the ESR spectroscopy, Mn^{4+} species was detected by the reaction of the Mn(acac)$_3$ and BzBr. On the basis of these results, we would propose the polymerization mechanism as shown in Scheme 3, although the detailed mechanism is not confirmed. One initiating radical was formed from Mn(acac)$_3$ (eq1), where the Mn(II) was produced and it was reacted with Mn(IV) , and Mn(III) was recovered (eq7). In another radical the amount of the initiation from acac was small as compared with that from R derived from BzBr (eq2), and the initial end was determined by NMR spectroscopy when MBP was used instead of BzBr. Slow initiation causes a broad molecular weight distribution of the polymer. However, the molecular weight of polymer can be controlled in the polymerization of St with Mn(acac)$_3$-BzBr, since the propagation proceeds through a similar mechanism to the transition metal mediated living radical polymerizations (eq4~6).



Scheme 3 Polymerization mechanism of St with Mn(acac)$_3$-RX

References and Notes

1. Matyjaszewski,K. Ed. "Controlled Radical Polymerization" American Chemical Society Washington DC (1997) Vol.685.
2. (a) Georges,M.K. Veregin,R.P.N. Kazmaier,P.M. Hamer,G.K. (1994) Trends Polym 2: 66.
   (b) Georges,M.K. Veregin,R.P.N. Kazmaier,P.M. Hamer,G.K. (1993) Macromolecules 26: 2987.
   (c) Georges,M.K.N. Veregin,R.P. Hamer,G.K. Kazmaier,P.M.(1994)Macromol Symp 88: 89.
   (d) Malmstrom,E.E Hawker,C.J. (1998) Macromol Chem Phys 199: 923.
   (e) Ohno,K. Tsuji,T. Fukuda,T. (1997) Macromolecules 30: 2503.
   (f) Ohno,K. Goto,A. Fukuda,T. Xia,J. Matyjaszewski,K. (1998) Macromolecules 31: 2699.
   (g) Fukuda,T. Goto,A. Ohno,K. (2000) Macromol Raipd Commun 21: 151.
   (h) Moad,G. Rizzardo,E. (1995) Macromolecules 28: 8722.
   (i) Hawker,C.J. (1997) Acc Chem Res 30: 373.
   (j) Yoshida,E. (1996) J Polym Sci Part-A Polym Chem 34: 2937.
3. Kato,M. Kamigaito,M., Higashimura,T. (1995) Macromolecules, 29,1721.
4. Wang,J.-S. Matyjaszewski,K. (1995) J Am Chem Soc 117: 5614.
5. (a) Chiefari,J. Chong,Y.K. Ercole,F. Kristina,J. Jeffery,J. Le,T.P.T. Mayadunne,R.T.A. Meijs,G.F. Moad,C.L. Moad,G. Thang,S.H. (1998) Macromolecules 31:5559
   (b) Chong,Y.K. Lee,T.P. Moad,G. Rizzardo,E. Thang,S.H. (1999) Macromolecules 32: 2071.
   (c) Mayadunne,R.T.A. Rizzardo,E. Chiefari,J. Chong,Y.K. Moad,G. Thang,S.H. (1999) Macromolecules 32: 6977.
   (d) Mayadunne,R.T.A. Rizzardo,E. Chiefari,J. Krstina,J. Moad,G. Postma,A. Thang,S.H. (2000) Macromolecules, 33: 243.
6. (a)Otsu,T. Yoshida,M. (1982) Makromol Chem Rapid Commun 3: 127.
   (b)Otsu,T. Yoshida,M. Tazaki,T. (1982) Makromol Chem Rapid Commun 3: 133.
   (c) Otsu,T. Kuriyama,A. (1984) Eur Polym J 25: 643.
   (d) Otsu,T. Kuriyama,A. (1984) Polym Bull 11: 135.
   (e) Otsu,T. Ogawa,T. Yamamoto,T. (1986) Macromolecules 19: 287.
   (f) Otsu,T. Kuriyama,A. Yoshioka,M. (1989), Eur Polym J 25: 643.
   (g) OtsuT. Tazaki,T. (1986) Polym. Bull 16: 277.
   (h) Otsu,T.; Matsumoto,A. (1998) Adv Polym Sci 136: 75.
7. Ueigaki,H Kotani,Y. Kamigaito,M. Sawmoto,M. (1997) Macromolecules 30, 2249.
8. Granel,C. Dubois,Ph. Jerome,R. Teyssie,Ph. (1997) Macromolecules 30: 8576.
9. Lecomte,Ph. Drapier,I. Dubius,Ph. Teyssie,Ph. (1997) Macromolecules 30: 7631.
10. Ando,T. Kamigaito,M. Sawamoto,M. (1997) Macromolecules 30: 4507.
11. Kastning,E.G. Naarmann,H. Reis,H. Berding,C. (1965) Angew Chem 77: 313.
12. Otsu,T. Minamii,N. Nishikawa,Y. (1968) J.Macromol. Sci. Part A-2: 905.
13. Kotani,Y. Kato,M. Kamigaito,M. Sawamoto,M. (1996) Macromolecules 29: 6979.
14. Lewis,F.M. Walling,C. Cummings,W. Briggs,E.J. Wenisch,W.J. (1964) J Am Chem Soc 84:3824
15. Inoue,Y. Nishioka,A. Chujo,R. (1972) Makromol Chem 156,207.
16. Gaynar,S.G., Edelman,S., Matyjaszewski,K. (1996) Macromolecules 29: 1079.