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Anionic polymerization of 2-(*N*-carbazolyl)ethyl methacrylate

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Abstract

The homopolymer, poly(CzMA), with controlled molecular weight (MW) and narrow molecular weight distributions (MWD) was successfully synthesized by using (1,1,4,4-tetraphenylbutanediyl)dipotassium and diethylzinc (Et_2Zn) in THF at various temperatures, 25, −45, and −78 °C, under high vacuum conditions. The Et_2Zn acted both as a protective group through the formation of coordination with ester enolate anion and as a scavenger to remove impurities. Block copolymers, poly(CzMA-*b*-styrene-*b*-CzMA) and poly(MMA-*b*-CzMA-*b*-MMA), with narrow MWD were also successfully synthesized by sequential anionic living polymerization. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Anionic polymerization; CzMA; Diethylzinc

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1. Introduction

The anionic polymerization of methacrylate derivatives has problems such as ester carbonyl attacks of the anionic initiators and propagating chain ends as well as an intramolecular termination [1]. The control of reaction temperature, the choice of initiator, solvent, and additives are important to suppress the inherent ester carbonyl attack and the intramolecular termination [1–5]. There are several successful attempts in this direction involving different additives such as LiCl [6], TMEDA [7], spartein/9-fluorenyl lithium [8], tetraalkylammonium salts [9,10], diethylzinc [11–13] and triethylborane [14]. All these systems are based on the coordination of the additives to the ester enolate [15–25]. LiCl can be formed the lithium ester enolate with methacrylate. The complex between LiCl and ester group decreases both the reaction rate and side reaction [5–6] thus reduce the side reaction. TMEDA participates in the exchange reaction during the polymerization [7]. The exchange equilibrium will affect the stability of the growing chain ends. Coordination of diethylzinc or triethylborane with carbonyl group produces stable propagating species that affords well-defined polymers [11–14].

First attempt of the controlled anionic polymerization of the methacrylate derivatives was by Teyssie et al. by using LiCl at −78 °C in THF for the polymerization of *tert*-butyl acrylate and methacrylate with quantitative yields and relatively narrow MWD [6]. Also, Müller and coworkers reported polymerization of *n*-butyl acrylate in the presence of aluminum alkyls in toluene and aluminum alkyl-Lewis base in toluene at −78 °C [15–17]. Hogen-Esch et al. reported polymerization results of MMA at ambient temperatures in the presence of tetraphenylphosphonium cation in high yields with narrow MWD ($M_w/M_n \leq 1.2$) [18]. Hatada et al. reported the polymerization results of methacrylate by using alkyl aluminum phenoxide at 30 °C in quantitative yield. However, the MWD was broad [19].

Recently, Nakahama et al. reported the polymerization results of acrylate and methacrylate derivative with alkynyl group in the presence of Et_2Zn in THF at −78 °C. They reported that the addition of Et_2Zn to the reaction solution lowers the polymerization rates and enhances the persistency of the anionic propagating ends due to the coordination of Et_2Zn to the enolate anions at the propagating end groups [11–13]. Furthermore, they reported the polymerization results of acrylate derivatives in THF at room temperature by using triethylborane having narrow MWD ($M_w/M_n \cong 1.2$) with quantitative yields [11–13].

In this paper, the results from anionic homopolymerizations and copolymerization of 2-(*N*-carbazolyl)ethyl

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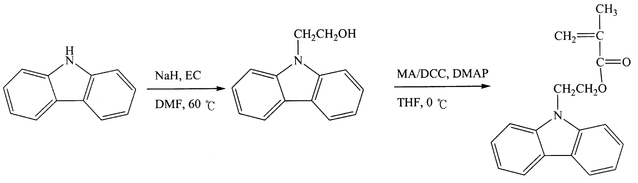

Scheme 1.

methacrylate (CzMA) with styrene or MMA in the presence of Et_2Zn are reported. Et_2Zn can react with protic impurities, but cannot polymerize methacrylate monomers. Therefore, Et_2Zn is effective additive for the purification of high boiling point monomers. The presence of carbazole is essential in the polymer to exhibit optical properties [26–28]. Here we report, however, not the optical properties but only the polymerization results of CzMA.

2. Experimental

2.1. Materials

Carbazole (Acros) was purified by crystallization from ethyl alcohol (Fisher Scientific Co.) solution before use. Methacrylic acid (Aldrich) was purified by passing through an alumina column before use. Diethylzinc (Et_2Zn) was purchased from Aldrich and used without further purification. Other chemicals were used without further purifications. Styrene (Aldrich) was passed through an alumina column, washed with aqueous NaOH solution to remove inhibitors, then rinsed with water, dried for 24 h over $MgSO_4$ and distilled at 25 °C under reduced pressure. Methyl methacrylate (MMA, Aldrich) was purified by alumina column, washed with 5% NaOH and then with water. It was dried first over $MgSO_4$ and then over CaH_2 for 48 h and distilled over CaH_2 under reduced pressure prior to use. Commercially available 1,1-diphenyl ethylene (DPE) was dried over CaH_2 and distilled over CaH_2. LiCl was dried under high vacuum (10^{-6} mmHg) for 3 days with baking for every 1 h equipped with break-seal, and diluted using THF. Free metal naphthalenides, Li- and K-naphthalenide, were prepared by the reactions of a small excess amount of naphthalene with the corresponding alkali metal at room temperature in THF. The initiator was stored at −30 °C in ampules equipped with break-seals. The concentration of metal naphthalenide was determined by colorimetric titration to colorless end point with *n*-octyl alcohol in a sealed reactor through break seals under high vacuum at room temperature.

2.2. Synthesis of monomer

2.2.1. 2-(N-carbazolyl)ethyl methacrylate (CzMA)[1] [29]

Sodium hydride (NaH, 17.3 g, 0.718 mol) was slowly added to carbazole (100 g, 0.599 mol) dissolved in dimethyl formamide (DMF, 1000 ml) at room temperature. After addition of NaH, ethylene carbonate (EC, 64.0 g, 0.727 mol) was added to the reaction mixture. The reaction mixture was mechanically stirred at 60 °C for 12 h, poured into NaOH aqueous solution, and filtered. The filtered solid was crude 9-hydroxyethyl carbazole that was purified by column separation using diethyl ether and hexane (volume ratio 3:7). 9-Hydroxyethylcarbazole (50.0 g, 0.246 mol) was reacted with methacrylic acid (36.9 g, 0.369 mol) in THF (500 ml) using dicyclohexylcarbodiimide (DCC, 101 g, 0.492 mol) and dimethylaminopyridine (DMAP, 60.0 g, 0.492 mol) as catalysts at ice temperature for 5 h. The resulting mixture was filtered to remove the salts after storing in a refrigerator and then extracted with water and diethyl ether. The ether solution was then evaporated under reduced pressure. The solid was dissolved in ethanol and recrystallized. The products were characterized by FT-IR, ^1H- and ^{13}C-NMR spectroscopy.

mp 80 °C; ^1H NMR (DMSO-d_6): $\delta = 8.2, 7.6, 7.5, 7.1$ (m, phenyl), 5.5, 5.7 (d, CH_2=), 4.7 (t, –N–CH_2–), 4.5 (t, –CH_2–O–), 1.9 (s, –CH_3); ^{13}C NMR (DMSO-d_6): $\delta = 168$ (–*C*=O), 135 (CH_2=*C*–), 125 (*C*H_2–C–), 109, 118, 120, 122, 125, 140 (phenyl), 63 (–N–*C*H_2–), 17 (–*C*H_3); IR(KBr): 1740 cm^{-1} (C=O); Yield 90% (Scheme 1).

2.3. Anionic polymerization of CzMA

The anionic polymerization was carried out in THF under high-vacuum conditions (10^{-6} mmHg) for 5 min to 4 h in an all-glass apparatus equipped with break-seals in the usual manner. Monomer, initiator, and additive solution were prepared and divided in THF under high vacuum condition. Et_2Zn solution was introduced into the monomer in THF solution before polymerization for coordination with the carbonyl group and to remove impurities in the monomers.

For the homopolymerization of CzMA, a THF solution of 1,1-diphenylethylene (DPE) was added to metal naphthalenide (Li- or K-naph) solution in THF at −78 °C and allowed to react for 30 min at −78 °C. CzMA with Et_2Zn was added to the initiator in THF solution, polymerized for 5 min to 4 h at 25, −45, and −78 °C, and then terminated with methanol. For the polymerization of CzMA at 25 °C, the CzMA solution was introduced to (1,1,4,4-tetraphenylbutanediyl)dipotassium solution at −78 °C, and then polymerized at 25 °C. The red color of (1,1,4,4-tetraphenylbutanediyl)dipotassium (or lithium) anions changed immediately to pale yellow after adding CzMA. The pale yellow color was retained during the anionic polymerization of CzMA in THF at −78 °C for 3 h.

^1H NMR ($CDCl_3$): $\delta = 7.8$–8.2, 6.9–7.5 (phenyl), 3.9–4.1 (–CH_2CH_2–), 1.2–2.0 (–CH_3), 0.0–0.5 (–CH_2–C–); IR (KBr): 1740 cm^{-1} (C=O); T_g 117 °C; T_d 291 °C.

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[1] This work was presented in part at the 218th ACS National Meeting, Washington, Aug 2000 [30].

2.4. Block copolymerization of CzMA with styrene and MMA

2.4.1. Poly(CzMA-b-styrene-b-CzMA)

Styrene was initiated with K-naph in THF at −78 °C in an all glass apparatus in vacuo. After 30 min, a portion of living polystyrene was withdrawn to an attached receiver to determine the characteristics of the homopolymer. A DPE solution was then added to the living polystyrene solution in THF at −78 °C and allowed to react for 30 min at −78 °C. CzMA with Et_2Zn in THF solution was added to the living homopolymer solution, and polymerized for 3 h at −78 °C. The characteristic red color of polystyryldipotassium and polystyryl end capped with 1,1-diphenylethanepotassium changed to a pale yellow color after adding the CzMA in THF solution.

^{1}H NMR ($CDCl_3$): $\delta = 7.8$–8.2, 6.9–7.5, 6.2–6.8 (phenyl), 3.7–4.4 (–CH_2CH_2–), 1.2–2.0 (–CH_3), 0.0–0.5 (–CH_2–C–); IR (KBr): 1740 cm^{-1} (C=O).

2.4.2. Poly(MMA-b-CzMA-b-MMA)

A DPE solution dissolved in THF was added to the K-naph solution in THF at −78 °C and allowed to react for 30 min at −78 °C. The first-stage polymerization of CzMA with Et_2Zn was initiated with (1,1,4,4-tetraphenylbutanediyl)dipotassium in THF at −78 °C. After 3 h, a portion of a living polymer was withdrawn to an attached receiver. MMA in THF without Et_2Zn was then added to the residue of the polymer solution, and the mixture was reacted for 3 h at −78 °C to complete the second-stage polymerization. The red color of the (1,1,4,4-tetraphenylbutanediyl)dipotassium changed immediately to a pale yellow color by adding CzMA and changed to a pale yellow after adding MMA.

Poly(MMA-b-CzMA-b-MMA): ^{1}H NMR ($CDCl_3$): $\delta = 7.8$–8.2, 6.9–7.5 (phenyl), 3.7–4.4 (–CH_2CH_2–), 1.2–2.0 (–CH_3), 0.0–0.5 (–CH_2–C–); IR (KBr): 1740 cm^{-1} (C=O).

2.5. Characterization

All the polymers synthesized in this report were precipitated in large amounts of methanol, dried, dissolved in benzene, and filtered to remove zinc compounds. The filtered clear polymer solution was freeze-dried. The polymers were characterized by size exclusion chromatography (SEC, Waters M 77251, M510). Molecular weights (MW) of the polymers were estimated by using SEC with four columns (HR 0.5, HR 1, HR 3 and HR 4, Waters Styragel columns run in series. The pore size of the columns is 50, 100, 10^3 and 10^4 Å, respectively.) with a refractive index detector at a flow rate of 1 ml min^{-1} using THF as elution solvent, at 40 °C and calibrated with PMMA standards (American Polymer Standards Corp.). Also, the polymer was characterized by ^{1}H FT-NMR (JEOL JNM-LA300WB 300 MHz ^{1}H), and FT-IR (Perkin Elmer System 2000). Thermal properties were characterized by TGA (TA-2050) and DSC (TA2010) at heating rate 10 °C min^{-1}.

3. Results and discussion

3.1. Homopolymerization of CzMA

Table 1 shows the polymerization results of CzMA with (1,1,4,4-tetraphenylbutanediyl)dilithium initiator (runs 1 and 2), prepared in situ from Li-naph and DPE, in THF at −78 °C in the presence of LiCl. The reaction yield is low due to the low initiation efficiency. Because impurities, such as water, still remain in the monomers even dried in vacuo for 1 week, the reaction yield does not increase linearly with increase in reaction time. LiCl can protect the carbonyl group from attack by the carbanion, however, it cannot remove the impurities which act as scavengers of the initiators. For that reason, the observed MW is higher than the predicted MW. Also, the molecular weight distributions (MWD) are still broad, $M_w/M_n > 1.2$.

To increase the efficiency of the initiator, Et_2Zn solution was directly introduced into the monomer in THF solution before polymerization for coordination with the carbonyl groups and to remove impurities in the monomers [11–13]. There are two possibilities to coordinate Et_2Zn with CzMA; coordination with vinyl and carbonyl group. If Et_2Zn coordinate with carbonyl group, it will be increased the propagation rate during the polymerization due to the electron withdrawing effect by Et_2Zn. The electron withdrawing effect of the Et_2Zn coordinated with carbonyl group increase positive charge of the β carbon. Therefore, initiation of the CzMA coordinated with Et_2Zn in carbonyl group is much easier than that of CzMA coordinated with Et_2Zn in vinyl group. Also, the Et_2Zn can coordinate with propagating end during the polymerization. However, the propagation rate constant of poly(CzMA) will be decreased due to the electron withdrawing effect of Et_2Zn, if Et_2Zn coordinate with ester carbonyl group of the chain end.

The polymerization of CzMA with Et_2Zn was very slow and quantitative within 3 h at −78 °C in the presence of a 10-fold excess of Et_2Zn based on initiator (runs 3–9). This may be due to the retardation of the reaction rate by Et_2Zn coordination with ester carbonyl groups in reactive chain end [11–13]. The coordination of the Et_2Zn with carbonyl group is confirmed by ^{13}C-NMR. In ^{13}C-NMR spectra, the carbonyl carbon resonance peak of the CzMA in THF solution was shifted completely from 167.5 to 166.9 ppm by adding Et_2Zn under high vacuum conditions [29–31]. The carbonyl carbon resonance peak of the CzMA is shifted to a higher frequency due to the coordination with Et_2Zn. Therefore, Et_2Zn was coordinated with carbonyl group of the CzMA by introducing Et_2Zn before polymerization. However, Et_2Zn was also coordinated with ester carbonyl group of the reactive chain end during polymerization resulting retardation of reaction rate. Also, the quantitative

Table 1
Anionic polymerization of CzMA in THF at various temperatures with (1,1,4,4-tetraphenylbutanediyl)dipotassium initiator as a function of time in the presence of Et_2Zn

Run	Amount of reagent (mmol)				Temp (°C)	Time (min)	Yield (%)	$M_n \times 10^{-3}$		M_w/M_n[a]
	Initiator	DPE	Additive	CzMA				Calcd[b]	Obsd[a]	
1	0.060[c]	0.110	3.247[d]	1.190	−78	60	87	9.5	8.0	1.22
2	0.110[c]	0.150	3.658[d]	2.830	−78	180	62	9.0	15.0	1.24
3	0.104	0.135	1.565	2.391	−78	15	14	2.0	2.5	1.24
4	0.099	0.135	1.365	2.086	−78	30	35	4.0	3.5	1.21
5	0.091	0.120	1.208	1.918	−78	60	58	5.8	5.0	1.19
6	0.086	0.137	0.987	1.560	−78	90	74	7.5	7.5	1.20
7	0.091	0.133	1.440	2.204	−78	120	86	11.5	10.0	1.20
8	0.096	0.117	1.798	2.855	−78	180	100	16.0	15.0	1.09
9	0.113	0.150	1.974	3.742	−78	180	100	18.5	18.0	1.07
10	0.104	0.129	0.574	1.833	−45	15	16	1.7	2.0	1.43
11	0.092	0.109	0.573	1.876	−45	30	40	4.0	5.0	1.35
12	0.082	0.109	0.585	1.917	−45	60	71	7.5	8.5	1.35
13	0.094	0.137	0.554	1.815	−45	90	80	9.0	12.0	1.32
14	0.093	0.123	0.492	1.611	−45	120	100	10.0	15.0	1.30
15	0.107	0.134	1.480	1.856	−45	120	100	10.0	13.0	1.31
16	0.096	0.124	0.720	1.842	25	5	13	1.6	2.8	1.34
17	0.100	0.177	1.054	1.692	25	10	56	5.5	12.0	1.38
18	0.095	0.180	1.243	1.996	25	30	99	11.6	17.0	1.23
19	0.134	0.137	1.162	1.866	25	60	100	8.0	11.0	1.41
20	0.087	0.117	1.085	1.450	25	120	100	9.5	13.0	1.35

[a] M_n (obsd) and M_w/M_n were obtained by SEC calibration using standard PMMA in THF at 40 °C.
[b] M_n (calcd) = (M_w of CzMA) × 2 × [CzMA]/[K-naph.] × yield.
[c] Li-naph. was used as an initiator.
[d] LiCl was used as an additive.

yield was obtained for 3 h, because all the protic impurities removed by adding Et_2Zn in the monomer. It means that high boiling point and solid monomers difficult to be purified by distillation could be purified by adding the additive.

The reaction yields increase with increasing reaction time. The observed MW determined by SEC using PMMA standard is in good agreement with the calculated value. This indicates that the impurities were removed by adding Et_2Zn into the monomer. Also, a narrow M_w/M_n, less than 1.1 (Fig. 1), was observed, after complete polymerization. The coincided MW even though it is not absolute value and narrow MWD indicates the living nature of the polymerization. As shown in Fig. 1, as the amount of monomer is gradually decreased, the MW of the polymer increased with increase in reaction time. Furthermore, the longer the reaction time, the sharper the SEC peak became. The elimination of Et_2Zn from the resulting polymers by filtering out the Et_2Zn in benzene solution was confirmed by using energy dispersed X-ray (EDX). The spectrum shows that there are no zinc compounds in the polymer. This means that Et_2Zn was coordinated with the monomers weakly and was perfectly removed by reaction with methanol during the termination reaction.

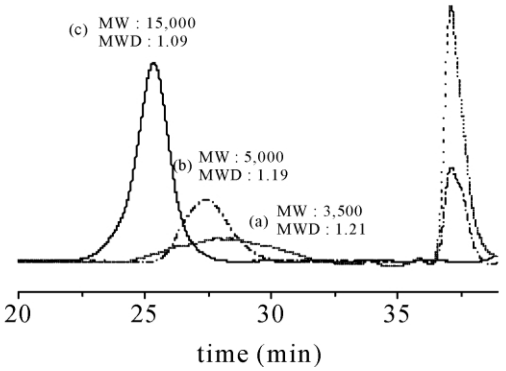
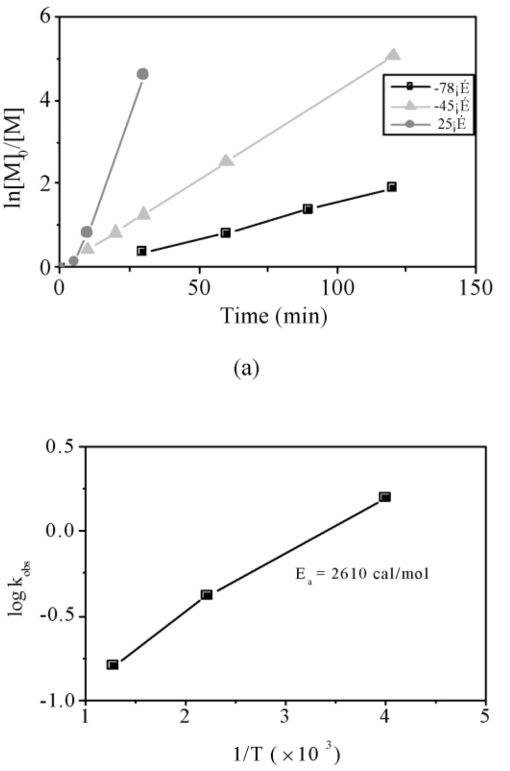


Fig. 1. SEC profile of poly(CzMA) synthesized in THF at −78 °C with (1,1,4,4-tetraphenylbutanediyl)dipotassium initiator as a function of time in the presence of Et_2Zn (a) 30 min, (b) 60 min, and (c) 180 min.

The polymerization of CzMA with (1,1,4,4-tetraphenylbutanediyl)dipotassium in THF at −45 °C in the presence of 5- to 15-fold excess of Et_2Zn based on initiator was quantitative within 90 min (runs 10–14). The reaction yield gradually increased with time. The polymerization rate of the CzMA at −45 °C is faster than that of the CzMA at −78 °C. The observed MW is higher than the calculated MW and a relatively broad MWD is obtained compared to polymerization results at −78 °C. This suggests that the side reactions, such as ester carbonyl attack, occurred by propagating end groups due to the weak coordination of Et_2Zn with carbonyl group at higher temperature. However, it is still possible to get polymer with quantitative yield and a relatively narrow MWD.

The polymerization of CzMA proceeded quantitatively within 30 min at 25 °C (runs 15–20). The reaction rate at 25 °C is faster than those of the CzMA at −45 and −78 °C.



(a)

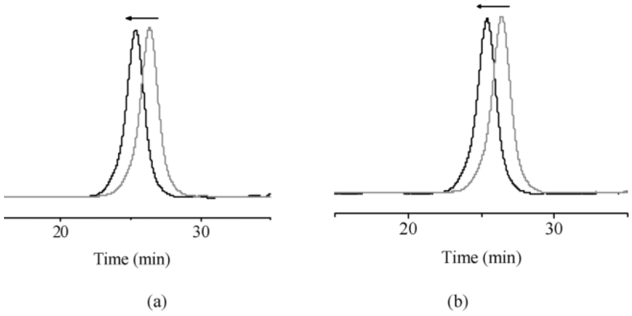
(b)

Fig. 2. First order time-conversion plots (a) and temperature-propagation constant plot (b) of the anionic polymerization of CzMA in THF at various temperatures in the presence of Et_2Zn.

This may be due to the weaker coordination of Et_2Zn with the ester enolate anions at the propagating end groups caused by increasing the polymerization temperature. The MWD of the polymers polymerized at −45 and 25 °C is broader than the that of the polymers polymerized at −78 °C. Also, the observed MW is higher than the calculated value due to side reactions. It is suggested that side reactions occurred at the reactive chain end during polymerization at higher temperatures.

3.2. First-order kinetic analysis

Fig. 2 shows time-conversion plots of the CzMA in THF at 25, −45, and −78 °C in the presence of Et_2Zn. The conversion of the CzMA gradually increased with time. About 30 min at 25 °C, 90 min at −45 °C, and 180 min at −78 °C is required to get a quantitative yield of the polymer. Even though the reaction temperature is increased from −78 to −45 °C, the reaction rate of CzMA is not very fast. The slopes of the $\ln[M_0]/[M]$ vs. t plots, (where $[M_0]$ is initial concentration of monomer, and $[M]$ is concentration of monomer at reaction time, t) are the propagation rate constants of the reactions at the various temperatures. The propagation rate constants of CzMA at −78, −45 and 25 °C are around 0.16 and 0.42, 1.60 l mol^{-1} min^{-1}, respectively.



(a)

(b)

Fig. 3. SEC profile of poly(CzMA-*b*-styrene-*b*-CzMA) (a) and poly(MMA-*b*-CzMA-*b*-MMA) (b) synthesized in THF at −78 °C in the presence of Et_2Zn.

The propagation rate constant at 25 °C is 10 times greater than the propagation rate constant at −78 °C. This may be due to the weakening of the coordination of diethylzinc with the ester enolate anions at the propagating end groups by the increasing polymerization temperature. Fig. 2(b) shows temperature-propagation constant plot of CzMA in THF in the presence of Et_2Zn. The activation energy of the reaction, calculated by the Arrhenius equation, is 2610 cal mol^{-1}.

3.3. Block copolymerization of CzMA with styrene or MMA

The living polymer character of CzMA allows controlled block copolymerizations with other monomers by sequential monomer addition. Table 2 shows the results of block copolymerization of CzMA with styrene and MMA in the presence of Et_2Zn. The observed MW agreed with the calculated MW and the MWD was narrow, around 1.10 in poly(CzMA-*b*-styrene-*b*-CzMA) (runs 21 − 23 in Table 2, Fig. 3(a)). The living poly(CzMA) capped with 1,1-diphenylethanepotassium can successfully initiate polymerization of the second monomer, CzMA, without side reaction. Also, the side reaction during post polymerization is completely suppressed by using Et_2Zn.

The observed MW of the block copolymer is almost the same as the calculated MW and the MWD of the poly (MMA-*b*-CzMA-*b*-MMA) is narrow, less than 1.1 (runs 24–26 in Table 2, Fig. 3(b)). It is still possible to get a block copolymer with controlled MW and narrow MWD, even when Et_2Zn is not introduced into the MMA solution, second monomer. This is because the side reaction is completely suppressed by adding Et_2Zn into the first monomer solution. The Et_2Zn in the CzMA solution also acted as an additive during polymerization of the MMA. From these results, one concludes that the Et_2Zn acted as an additive at the growing chain ends.

4. Conclusions

Poly(CzMA) with controlled MW and narrow MWD was successfully synthesized in THF at 25, −45 and −78 °C by using coordination of Et_2Zn with ester enolate. The reaction

Table 2
Block copolymerization of CzMA with styrene, or MMA, in THF at −78 °C in the presence of Et_2Zn

Run	Amount of reagent (mmol)							Yield (%)	$M_n \times 10^{-3}$		M_w/M_n [a]
	K-naph	St	DPE	Et_2Zn	CzMA	MMA	M_1/M_2		Calcd [b]	Obsd [a]	
21	0.081	4.097	0.104	0.990	1.144		3.58 [c]	100	19	20	1.11
22	0.091	3.697	0.144	0.548	1.795		2.06 [c]	100	20	20	1.10
23	0.090	4.097	0.150	0.498	1.632		2.51 [c]	100	20	21	1.11
24	0.097		0.136	0.720	1.842	4.742	2.57 [d]	100	20	20	1.08
25	0.100		0.131	0.960	2.498	4.195	1.68 [d]	100	24	25	1.08
26	0.102		0.134	0.786	2.165	4.831	2.23 [d]	100	22	21	1.09

[a] M_n (obsd) and M_w/M_n were obtained by SEC calibration using standard PMMA in THF at 40 °C.

[b] M_n (calcd) = (M_w of CzMA) × 2 × [CzMA]/[K-naph.] × yield.

[c] M_1/M_2 = [St]/[CzMA].

[d] M_1/M_2 = [MMA]/[CzMA].

rate of CzMA at −78 °C in the presence of Et_2Zn is slower than the reaction rates at −45 and 25 °C due to the strong coordination of Et_2Zn to the enolate anion.

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References

[1] Szwarc M, Beylen MV. Ionic polymerization and living polymers. London: Chapman & Hall, 1993.
[2] Ozaki H, Hirao A, Nakahama S. Macromolecules 1992;25:1391–5.
[3] Szwarc M. Living polymers and mechanisms of anionic polymerization. Berlin: Springer, 1983.
[4] Morton M. Anionic polymerization: principles and practice. New York: Academic Press, 1983.
[5] Hsieh HL, Quirk RP. Anionic polymerization. New York: Marcel Dekker, 1996.
[6] Wang JS, Jerome R, Teyssie P. Macromolecules 1994;27:4902–7.
[7] Baskaran D, Chakapani S, Sivaram S. Macromolecules 1995;28:7315.
[8] Liu W, Yung Y, Chen C, Chen Y, Xi F. Macromol Chem Phys 1997;198:279–90.
[9] Novakov CP, Tsvetanov CB. Macromol Rapid Commun 1995;16:741–7.
[10] Baskaran D, Chakrapani S, Sivaram S, Hogen-Esch TE, Müller AHE. Macromolecules 1999;32:2865–71.
[11] Ishizone T, Uehara G, Hirao A, Nakahama S, Tsuda K. Macromol Chem Phys 1998;199:1827–34.
[12] Ozaki H, Hirao A, Nakahama S. Macromol Chem Phys 1995;196:2099–111.
[13] Ishizone T, Yoshimura K, Hirao A, Nakahama S. Macromolecules 1998;31:8706–12.
[14] Ishizone T, Yoshimura K, Yanase E, Nakahama S. Macromolecules 1999;32:955–7.
[15] Schmitt B, Schlaad H, Müller AHE, Mathiasch B, Steiger S, Weiss H. Macromolecules 2000;33:2887–93.
[16] Schmitt B, Schlaad H, Müller AHE. Macromolecules 1998;31:1705–9.
[17] Schmitt B, Schlaad H, Müller AHE, Jüngling S, Weiss H. Macromolecules 1998;31:573–7.
[18] Zagala AP, Hogen-Esch TE. Macromolecules 1996;29:3038–9.
[19] Kitayama T, Hirano T, Hatada K. Tetrahedron 1997;53:15263–80.
[20] Mori H, Hirao A, Nakahama S. Macromolecules 1994;27:35–39.
[21] Ohata M, Isono Y. Kobunshi Rombun Shu 1992;49:801–7.
[22] Nagasaki Y, Sato Y, Kato M. Macromol Rapid Commun 1997;18:827–35.
[23] Iijima M, Nagasaki Y, Kato M, Kataoka K. Polymer 1997;38:1197–202.
[24] Nagasaki Y, Nishizuka H, Tsuruta T. Polymer J 1995;27:959–62.
[25] Nagasaki Y, Ito H, Kato M, Kataoka K. Polym Bull 1995;35:137–42.
[26] Zhang Y, Wang L, Wada T, Sasabe H. Macromol Chem Phys 1996;197:667–76.
[27] Zhang Y, Wang L, Wada T, Sasabe H. Chem Commun 1996:559–62.
[28] Zhang Y, Hokari H, Wada T, Shang Y, Marder SR, Sasabe H. Tetra Lett 1997;38:8721–2.
[29] Cho YS, Lee JS. Macromol Rapid Commun 2001;22(8):638–42.
[30] Cho YS, Lee JS. Polym Prepr (Am Chem Soc Div Polym Chem) 2000;41(2):1223–4.
[31] Cho YS, Kim SW, Ihn CS, Lee JS. Polymer 2001;42(18):7611–6.