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Group Transfer Polymerization of Methacryl-Type Poly(2-oxazoline) Macromonomers

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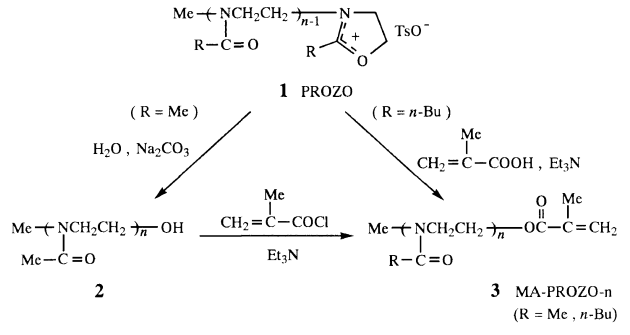
ABSTRACT: Group transfer polymerization (GTP) of methacrylate-terminated poly(2-alkyl-2-oxazoline) macromonomers (MA-PROZO-*n* **3**; R = Me and *n*-Bu; *n*, degree of polymerization) was examined using 1-methoxy-1-(trimethylsiloxy)-2-methyl-1-propene and nucleophiles as the initiator and catalyst, respectively, at 24 or 50°C. MA-PROZO-*n* **3** (R = *n*-Bu; *n* = 3, 14, and 31) was polymerized using tetra-*n*-butylammonium fluoride as the catalyst in tetrahydrofuran (THF) to provide poly(MA-PROZO-*n*)s (**4**; R = *n*-Bu) with M_n up to 37600. GTP of **3** (R = Me; *n* = 14 and 30) was carried out by use of KHF_2 as the catalyst in CH_3CN or CD_3CN to produce **4** (R = Me) with maximum M_n up to 17300. M_w/M_n of the **4** given from **3** of $n \geq 14$ was narrow (1.08—1.12). Rate of the GTP of the macromonomers **3** decreased with increase in *n* and concentrations of macromonomers. Maximum conversion of macromonomers **3** was obtained at relatively lower concentration of **3**, generally 89—95%. Polymer **4** (R = *n*-Bu) was coupled *in situ* with *p*-bis(bromomethyl)benzene or propagating species of living poly(2-*n*-butyl-2-oxazoline)s, to provide chain extended poly(MA-PROZO-*n*)s (**5**; R = *n*-Bu) or block copolymers (**6**). From characteristics of the reactivity of **3** and **4** and narrow molecular weight distribution of **4**, living nature of present polymerization was suggested.

KEY WORDS Macromonomer / Polyoxazoline / Group Transfer Polymerization / Living Polymerization / End-Capping / Block Copolymer /

Living poly(2-alkyl-2-oxazoline) (PROZO) (**1**) obtained by ring-opening polymerization[1] of 2-alkyl-2-oxazoline (ROZO) can be terminated by methacrylate anions to provide methacrylate-terminated PROZO macromonomers (MA-PROZO-*n* **3**; *n*, degree of polymerization of ROZO).[2] Macromonomers **3** have been synthesized by acylation of alcohols (**2**) produced by hydrolysis of **1**, with methacryloyl chloride.[2] PROZO **1** of poly(*N*-acylethylenimine) can be regarded as a polymer homologue of polar aprotic solvents such as *N*,*N*-dimethylacetamide, showing hydrophilic (R = Me, Et) or hydrophobic (carbon number of R $\geq$ 4) properties.[1] Amphiphilic copolymers have been synthesized by the copolymerization of **3** with methyl methacrylate or styrene.[3] Previously we examined radical polymerizability of **3**. The reactivity was strongly affected by carbon number of the alkyl groups and by PROZO chain length.[4] Reactivity in radical copolymerization of vinylbenzyl-terminated PROZO macromonomers with ordinary vinyl monomers was studied.[5]



Scheme 1.

Webster performed living polymerization of acrylic monomers initiated by silyl ketene acetals in the presence of a catalyst such as fluoride and bifluoride anion.[6] As for the group transfer polymerization (GTP) of macromonomers, Asami reported living GTP of methacrylate-terminated polystyrene macromonomers initiated by a silyl ketene acetal.[7] In the polymerization of the PROZO macromonomers, ionic nor ionic-like technique is not known, and should facilitate the production of living poly(macromonomer)s which may have narrow molecular weight distribution and may be utilized for introduction of functional groups. Radical polymerization seems not so easy to provide such living polymers.

The present paper describes GTP of MA-PROZO-*n* **3** (R = Me and *n*-Bu) and examination on living nature of the GTP and on utilization of the propagating species for a synthesis of block copolymers by termination with living PROZO and for chain extension by end-capping. This new method provides an amphiphilic graft polymer having hydrophobic methacrylate main chain and hydrophilic PROZO (R = Me) graft chain.

EXPERIMENTAL

Materials

Tetrahydrofuran (THF) and Et_2O were distilled over sodium wire. CH_3CN and CD_3CN were purified by distillation over P_2O_5. Solvents, $CHCl_3$, $CDCl_3$, petroleum ether, benzene, hexane, and methanol were distilled from molecular sieves. *N*,*N*-dimethylformamide (DMF) was distilled from CaH_2. 2-Methyl-2-oxazoline (MeOZO) was stirred with KOH and distilled. Methyl tosylate (MeOTs) and methacryloyl chloride were distilled *in vacuo*. Methacrylic acid and *p*-bis(bromomethyl)benzene (BMB) were dried with molecular sieves and distilled. 2-*n*-Butyl-2-oxazoline (BuOZO)[8] and 1-methoxy-1-

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(trimethylsiloxy)-2-methyl-1-propene (MTS)[9] were prepared according to the literature. Tris(dimethylamino)-sulfur(trimethylsilyl)difluoride (TASF), hexane solution (1.5 M) of *n*-butyl lithium and THF solution (1.0 M) of tetra-*n*-butylammonium fluoride (TBAF) were used as received. 1,1-Diphenyl-2-picrylhydrazyl (DPPH) was recrystallized from petroleum ether. KHF_2 was dried *in vacuo* at 150°C.

Measurements

^{1}H NMR spectra were recorded on a Jeol JNM FX60Q spectrometer with tetramethylsilane as the standard. IR spectra were measured by a Jasco IR-810 spectrophotometer. GPC analysis was performed using a Shimadzu LC-10AD chromatograph equipped with a Shimadzu RID-6A RI detector. For analysis of the products given from MA-PBuOZO-*n* (**3**), GPC columns, Shodex A-803 and Jasco Fine Pack Gel-101 were connected in series (Column A), and $CHCl_3$ was used as the eluent, while for analysis of the products given from MA-PMeOZO-*n* (**3**), two Tosoh TSK_{gel} GMH_{HR-M} columns were connected in series (Column B), and DMF was used as the eluent at 60°C, at a flow rate of 0.8 mL min^{-1} in all runs. Molecular weight data in GPC were obtained with PMeOZO standards.

Macromonomers

MA-PROZO-*n* (**3**) was prepared as follows (Scheme 1).[2] ROZO was heated with MeOTs initiator in CH_3CN at 80°C for 20 h to form living PROZO (**1**). 2-Oxazolinium salt at the chain end of **1** (R = Me) was hydrolyzed by heating with H_2O and Na_2CO_3 at 100°C for 20 h to give the PMeOZO-alcohols (**2**), which was acylated by methacryloyl chloride with Et_3N in CH_3CN to produce the MA-PMeOZO-*n* (**3**). On the other hand, MA-PBuOZO-*n* (**3**) was prepared by terminating the propagating species **1** (R = *n*-Bu) with methacrylic acid and Et_3N at 80°C. Macromonomers **3** were purified by reprecipitation from $CHCl_3$ solution with Et_2O (R = Me) or hexane (R = *n*-Bu) as non-solvents.

The results are shown in Table I. M_n of **3** was determined by both ^{1}H NMR and GPC. In ^{1}H NMR, signal integration ratios of NCH_2 protons (δ 3.4—3.6) to NCH_3 protons (δ 3.0) at ω ends gave the macromonomer chain length n (DP_n), from which M_n was calculated. GPC was measured through Column A described above in $CHCl_3$ as the eluent using PMeOZO standards prepared by the polymerization of MeOZO by MeOTs as the initiator. Molecular weight distributions of **3** were generally narrow reflecting living nature of the polymerization: $M_w/M_n = 1.12$—1.32. Functionality (F), *i.e.*, the number of methacrylate groups per molecules of **3** was determined from the signal integration ratios of vinyl protons (δ 5.60 and 6.03) in methacrylate groups to NCH_3 protons (δ 3.0) at ω end.

GTP of MA-PROZO Macromonomers (**3**)

a) MA-PBuOZO Macromonomers. Typical runs were as follows.

1) Polymerization of MA-PBuOZO-n (*Entry 5*): To a mixture of THF (6.6 mL), 0.167 g 0.96% MTS solution in THF (4.57×10^{-3} mmol), and 0.036 g 6.55×10^{-3} % solution of TBAF in THF (9.02×10^{-6} mmol) was added dropwise 2.804 g 6.99% solution of MA-PBuOZO-3 in THF (0.40 mmol) under argon, and the solution was heated at 50°C for 175 h in a sealed tube. The resulting solution was dried *in vacuo*, and the residue was dissolved in $CHCl_3$. The solution was added to hexane and the precipitate was collected, and dried giving 0.183 g of solid material. GPC analysis of the product gave macromonomer conversion to be 78%, M_n of poly(macromonomer) to be 23000 ($DP_n = 46.5$), and $M_w/M_n = 1.25$. ^{1}H NMR ($CDCl_3$): $\delta = 4.20$ (t, OCH_2–C–N), 3.58 (s, $CH_3OC=O$), 3.36 (br, NCH_2), 3.0 (br, NCH_3), 2.0—2.5 (br, $CH_2C=O$), 1.0—1.7 (br, CCH_2CH_2C), 0.93 (br, CH_3C).

Table I. MA-PROZO macromonomers (**3**)

Macromonomer **3**	M_n		DP_n[a]	M_w/M_n[a]	F[b]
	NMR	GPC			
MA-PMeOZO-14	1290	1250	13.5	1.12	0.98
MA-PMeOZO-30	2780	2630	29.7	1.17	0.98
MA-PBuOZO-3	510	490	3.0	1.32	1.00
MA-PBuOZO-14	1920	1840	13.7	1.13	1.00
MA-PBuOZO-31	4390	4020	30.8	1.19	0.99

[a] Determined by GPC using PMeOZO standards. [b] Functionality, determined by ^{1}H NMR.

2) Determination of Conversion by GPC (*Entry 1*): To a mixture of THF (7.2 mL), 0.882 g 0.96% MTS solution in THF (0.802 g; 4.86×10^{-2} mmol), and 0.190 g of 6.55×10^{-3} % solution of TBAF in THF (4.76×10^{-5} mmol) was added dropwise 3.448 g 6.99% solution of MA-PBuOZO-3 in THF (0.491 mmol) under argon, and the solution formed was divided in seven equal parts. Each part in a sealed tube was stirred at 24°C within the prescribed time interval and dried *in vacuo*. GPC analysis of the residues using $CHCl_3$ as the eluent gave macromonomer conversions p on the basis of following equation, under assumption that the peak area per unit weight of **4** was not different from that of macromonomers.

$$p = S_m/(S_p + S_m) \quad (1)$$

where S_p is the peak area of poly(MA-PROZO-*n*), and S_m is the peak area of MA-PROZO-*n*.

b) MA-PMeOZO Macromonomers. Typical runs were as follows.

1) Polymerization of MA-PMeOZO-n (*Entry 12*): A mixture of MA-PMeOZO-14 (0.132 g; 0.106 mmol), 0.247 g 0.74% MTS solution in CH_3CN (1.05×10^{-2} mmol), KHF_2 (0.077 mg; 9.91×10^{-4} mmol), and CH_3CN (11.5 mL) was heated at 50°C under argon for 235 h. The resulting solution was added to Et_2O to precipitate a polymeric material, which was dissolved in CH_3CN and filtered. The filtrate was added to Et_2O and the precipitate was dried *in vacuo* giving 0.125 g of solid material. GPC analysis of the product gave macromonomer conversion to be 82%, M_n of poly(macromonomer) to be 11220 ($DP_n = 8.8$), and $M_w/M_n = 1.12$. ^{1}H NMR (CD_3CN): $\delta = 4.22$ (t, OCH_2–C–N), 3.57 (s, $CH_3OC=O$), 3.38 (br, NCH_2), 2.96 (br, NCH_3), 2.0 (br, $CH_3C=O$).

2) Determination of Conversion by ^{1}H NMR (*Entry 11*): In a 5 mm o.d. NMR tube 0.025 g of MA-PMeOZO-

14 (2.00×10^{-2} mmol), 0.094 g 0.35% MTS solution in CD_3CN (1.89×10^{-3} mmol), KHF_2 (0.014 mg; 1.78×10^{-4} mmol), and CD_3CN (0.4 mL) were mixed under argon, sealed, and allowed to stand at 24°C within a prescribed time and chilled to quench at −78°C. Decrease of signal integration ratio of δ 5.04 and 5.59 ($CH_2=C$, methacryloyl) to δ 4.24 (t, OCH_2) in ^1H NMR gave macromonomer conversion.

Reaction of Living Poly(macromonomer)s (**4**)

a) Termination by BMB. To a mixture of THF (0.9 mL), 1.287 g 0.96% MTS solution in THF (7.09×10^{-2} mmol), and 0.277 g 6.55×10^{-3} % solution of TBAF in THF (6.95×10^{-5} mmol) was added dropwise 3.892 g 6.99% solution of MA-PBuOZO-3 in THF (0.555 mmol) under argon, and the solution was heated at 50°C for 48 h. GPC analysis of 0.2 mL aliquot gave macromonomer conversion as 82% and M_n of poly(macromonomer) to be 3500 ($DP_n=6.8$). To the reaction solution were added TASF (20.7 mg; 7.52×10^{-2} mmol) and BMB (9.3 mg; 3.54×10^{-2} mmol) at −78°C, and stirred for 24 h. The solution was dried *in vacuo*. The residue was dissolved in $CHCl_3$, precipitated in hexane, filtered, and dried to give 0.258 g of solid material. GPC analysis of the product gave conversion of the poly(macromonomer) to be 94% and M_n to be 8800. ^1H NMR ($CDCl_3$): $\delta=7.1$—7.3 (m, C_6H_4), 4.50 (s, $CH_2\phi$), 4.17 (t, OCH_2–C–N), 3.60 (s, $CH_3OC=O$), 3.40 (br, NCH_2), 3.0 (br, NCH_3), 2.0—2.5 (br, $CH_2C=O$), 1.0—1.7 (br, CCH_2CH_2C), 0.95 (br, CH_3C).

b) Termination by Living PBuOZO. To a mixture of THF (6.5 mL), 2.145 g 0.96% solution of MTS in THF (0.118 mmol), and 0.461 g 6.55×10^{-3} % solution of TBAF in THF (1.16×10^{-4} mmol) was added dropwise 14.845 g 6.99% solution of MA-PBuOZO-3 in THF (2.115 mmol) under argon, and the solution was heated at 50°C for 48 h. GPC analysis of 0.1 mL aliquot gave macromonomer conversion as 76% and M_n of poly(macromonomer) **4** to be 8200 ($DP_n=16.4$). Separately, a mixture of MeOTs (0.023 g; 0.124 mmol), BuOZO (0.207 g; 1.627 mmol; $[BuOZO]_0/[MeOTs]_0=13.1$), and CH_3CN (1.0 mL) was heated at 80°C for 24 h under argon to provide living PBuOZO (**1**). An aliquot (0.1 mL) was analysed by GPC using the Column A to give M_n to be 1820 ($DP_n=12.8$). To the polymerization solution given from MA-PBuOZO-3 were added TASF (0.035 g; 0.127 mmol) and a solution of **1** (R=*n*-Bu; $n=13$) at −78°C, and stirred for 24 h. The solution was dried *in vacuo*. The residue was dissolved in $CHCl_3$, precipitated in hexane, filtered, and dried to give 1.082 g of solid material. GPC analysis of the product gave conversions of living polymers to be 100% and M_n as 12600. ^1H NMR ($CDCl_3$): $\delta=4.14$ (t, OCH_2–C–N), 3.37 (br, NCH_2), 3.0 (br, NCH_3).

RESULTS AND DISCUSSION

Group Transfer Polymerization

GTP of MA-PROZO-*n* **3** was examined using MTS as the initiator. GTP of MA-PBuOZO-*n* is described below. The polymerization was carried out using TBAF as the catalyst in THF at 24 and 50°C. MA-PBuOZO-*n* was readily soluble in THF. Macromonomer concentration was around 40 or 9 mmol L^{-1}, and feed ratio of macromonomer to initiator ($[M]_0/[I]_0$) was close to 10 or 40. After the reaction, the polymerization mixture was dried *in vacuo*. The residue was dissolved in $CHCl_3$ and the solution was added to hexane to precipitate a mixture of poly(MA-PBuOZO-*n*)s (**4**) and unreacted macromonomers. By use of TASF as the catalyst, no polymerization took place. Molecular weights of the products and conversion were estimated by GPC using $CHCl_3$ assuming that the peak area per unit weight of **4** was not different from that of the macromonomers.

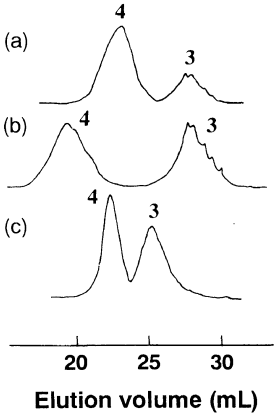


Figure 1. GPC curves of GTP products. (a) Entry 2: $[MA\text{-}PBuOZO\text{-}3]_0/[I]_0=10.1$; temp. 50°C; time, 24 h. Conversion = 76%. (b) Entry 5: $[MA\text{-}PBuOZO\text{-}3]_0/[I]_0=43.5$; temp. 50°C; time, 24 h. Conversion = 55%. (c) Entry 8: $[MA\text{-}PBuOZO\text{-}14]_0/[I]_0=9.8$; temp. 50°C; time, 48 h. Conversion = 39%. I, initiator (MTS).

In the case of MA-PMeOZO-*n*, GTP was examined using KHF_2 as the catalyst in CH_3CN or CD_3CN. THF could not be used for the reaction solvent because of poor solubility of MA-PMeOZO-*n*. The polymerization reaction was conducted with macromonomer concentration being around 40 or 9 mmol L^{-1}, and with feed ratio nearly 10 at 24 or 50°C. Molecular weights of the products were measured by GPC using DMF as the eluent. Polymerization could be observed only by KHF_2 as the catalyst, and was not detected by TASF or TBAF. This is consistent with GTP of methyl methacrylate.[10]

GPC curves of the products provided by GTP of MA-PBuOZO-*n* (**3**) are shown in Figure 1. Polymerization of MA-PBuOZO-3 with $[M]_0/[I]_0=43.5$ produced poly(MA-PBuOZO-3) **4** with higher molecular weight in lower conversion (55%) (b), but the polymerization of the same monomer with $[M]_0/[I]_0=10.1$ gave the polymer with lower molecular weight in higher conversion (76%) (a), showing increase in the feed ratio to decrease the polymerization rate, since the higher viscosity of polymerization system brought by higher molecular weight of produced polymer should depress more strongly the diffusion of growing sites and macromonomers to retard propagation reaction. MA-PBuOZO-14 gave **4** of higher molecular weight in lower conversion compared to MA-PBuOZO-3 at similar feed ratio (c). Longer chain length (n) of **3** should increase solution viscosity and segment density around growing ends to suppress the diffusion of reactants.

Time dependence of macromonomer conversion in the polymerization of MA-PBuOZO-*n* ($n=3$ and 14) and MA-PMeOZO-14 under macromonomer concentration

Table II. Group transfer polymerization of MA-PROZO macromonomers (**3**)[a]

Entry	3		$[M]_0$[b]		Cat.[c]	Temp	Time	Conversion[d]	M_n[d]	DP_n[d]	M_w[d]
	R	n	mmol L^{-1}	$[I]_0$		°C	h	%			M_n
1	n-Bu	3	40.8	10.1	TBAF	24	196	85	4730	9.3	1.41
2	n-Bu	3	40.8	10.1	TBAF	50	162	83	5860	11.6	1.88
3	n-Bu	3	8.8	10.7	TBAF	24	246	95	5760	11.4	1.28
4	n-Bu	3	40.8	43.5	TBAF	50	175	78	23000	46.5	1.25
5	n-Bu	3	8.8	40.1	TBAF	50	262	89	22100	44.7	1.23
6	n-Bu	14	41.5	9.8	TBAF	24	180	51	12300	5.8	1.09
7	n-Bu	14	41.5	9.8	TBAF	50	165	52	12100	6.3	1.11
8	n-Bu	14	8.5	10.2	TBAF	50	268	90	18200	9.8	1.10
9	n-Bu	31	40.3	9.8	TBAF	50	270	42	37600	9.3	1.08
10	Me	14	40.1	10.1	KHF_2	24	162	57	7050	5.5	1.10
11	Me	14	40.1	10.5	KHF_2	50	173	65[e]	9430	7.4	1.18
12	Me	14	9.0	10.1	KHF_2	50	235	89	12300	9.7	1.12
13	Me	30	9.0	10.1	KHF_2	50	240	63	17300	6.5	1.21

[a] Solvent: THF (R = n-Bu), CH_3CN (R = Me; Entry 10, 12, and 13), and CD_3CN (R = Me; Entry 11). [b] M, macromonomer **3**; I, initiator (MTS). [c] Cat.: catalyst; $[I]_0/[Cat]_0 = 1020$ (for TBAF) and 10.6 (for KHF_2). [d] Determined by GPC. [e] Determined by ^1H NMR.

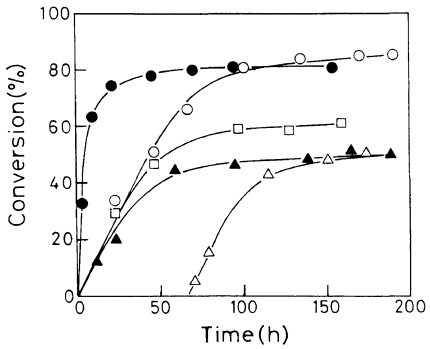


Figure 2. Time *versus* conversion plots in GTP of MA-PBuOZO-3 at 24 °C (Entry 1) (○), MA-PBuOZO-3 at 50 °C (Entry 2) (●), MA-PBuOZO-14 at 24 °C (Entry 7) (△), MA-PBuOZO-14 at 50 °C (Entry 8) (▲), and MA-PMeOZO-14 at 24 °C (Entry 11) (□).

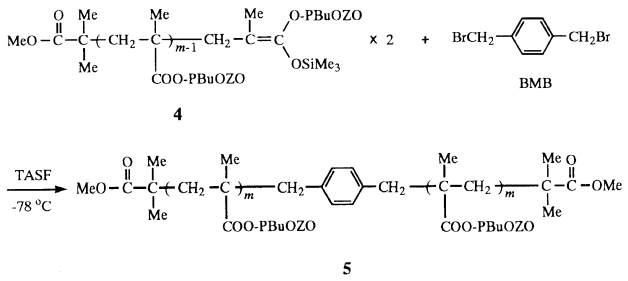
at 40 mmol L^{-1} at 24°C (R = Me and n-Bu) and 50°C (R = n-Bu) were examined (Figure 2). The polymerization of MA-PMeOZO-14 was conducted in a 5 mm o.d. NMR tube and conversion was determined by decrease of signal integration of vinyl-methylene protons of methacryloyl group to OCH_2 protons at the end of PMeOZO chain in ^1H NMR. The reactivity of MA-PROZO-n (**3**) was highly influenced by chain length and polymerization temperature. The polymerization rate decreased with increase in n, this being consistent with the inference from Figure 1. This is different from that in radical homopolymerization of vinylbenzyl-terminated PROZO macromonomers, in which polymerization rate increased with n, due to retardation of bimolecular termination caused by increase in segment density around propagating sites and solution viscosity.[11] The results for the present polymerizations may be ascribed mainly to depression of propagation reaction by suppression of interpenetration between propagating sites and macromonomers. Effects of the stable radical DPPH on the polymerization in same conditions as Entry 2 (Table II) were examined and this material was found to show no effects. Leveling off of the time *versus* conversion curves was generally observed, ascribable to suppression of the propagation reactions caused by depressing diffusion of growing chains and macromonomers mainly by increase in solution viscosity.

Polymerization rate at 50°C was generally higher than that at 24°C. Induction period was observed in a polymerization of MA-PBuOZO-14 at 24°C. The retardation of polymerization at 24°C seems due to depression of initiation step. In GTP of methyl methacrylate with MTS, the induction period has been observed and interpreted in terms of slow initiation.[12] MA-PBuOZO-31 could be polymerized under the same conditions at 50°C to produce **4**, but did not give any polymer at 24°C. These trends on reaction temperature can be explained that diffusion of growing chains and macromonomers is suppressed by drop of temperature. At −27°C, PROZO macromonomers could not be polymerized under the present conditions. Under different conditions, polymerization of MA-PMeOZO-14 at 24°C proceeded at higher rate than that of MA-PBuOZO-14 at 50°C.

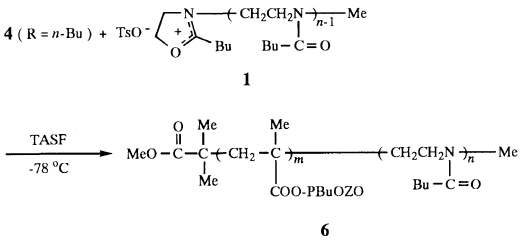
The results of GTP under various conditions are shown in Table II. DP_n of the poly(MA-PROZO-n)s **4** was generally close to the feed ratio ($[M]_0/[I]_0$), supporting the living nature of polymerization. Higher reaction temperature (50°C) increased polymerization rate, but also dispersion (M_w/M_n). Conversion of macromonomers **3** after enough reaction time increased with decrease in initial concentrations and decreased with increase in chain length n. Increase in macromonomer concentration should increase viscosity of polymerization system to retard propagation. Thus, monomer concentration close to 9 mmol L^{-1} gives higher conversion (89—95%) for all macromonomers. Molecular weight distribution of **4** obtained from the macromonomers **3** (≥ 14) was fairly narrow as described above, this being consistent with the living nature of present polymerization. Polymers from MA-PBuOZO-3 showed relatively higher M_w/M_n, due to broad dispersity of macromonomers.

Coupling Reactions of Poly(macromonomer)s

Coupling reactions of the poly(MA-PBuOZO-n)s **4** produced by GTP of MA-PBuOZO-3 and -14, by utilizing termination with BMB (Scheme 2) and living PBuOZO **1** ($n = 13$) (Scheme 3), were examined *in situ*. The latter reaction (Scheme 3) was mutual termination between living polymers to provide a block copolymer. These termination reactions were carried out in THF at −78°C



Scheme 2.



Scheme 3.

Table III. Termination of living poly(MA-PBuOZO-*n*)s (**4**) with BMB

Entry	Group transfer polymerization[a]						Termination[c]		
	MA-PBuOZO-*n*								
	n	Concentration / mmol L^{-1}	$[M]_0/[I]_0$	Time / h	Conversion[b] / %	M_n of **4**[b]	$[BMB]_0/[I]_0$	Conversion of **4**[b] / %	M_n of **5**[b]
14	3	83.2	7.9	48	82	3500	0.50	94	8800
15	14	41.2	9.4	96	50	10300	0.50	96	21300

[a] M, macromonomer **3**; I, initiator (MTS); solvent, THF; catalyst, TBAF ($[I]_0/[Cat]_0=1020$); temp, 50°C. [b] Determined by GPC. [c] $[TASF]_0/[I]_0=1.27$; temp, −78°C; time, 24 h.

Table IV. Termination of living poly(MA-PBuOZO-*n*)s (**4**) with living PBuOZO (**1**)

Entry	Group transfer polymerization[a]						Polymerization[c] of BuOZO		Termination[d]		
	MA-PBuOZO-*n*										
	n	Concentration / mmol L^{-1}	$[M]_0/[I]_0$	Time / h	Conversion[b] / %	M_n of **4**[b]	$[BuOZO]_0/[MeOTs]_0$	M_n of **1**	$[MeOTs]_0/[I]_0$	Conversion of **4**[b] / %	M_n of **6**[b]
16	3	86.3	17.9	72	74	8200	13.1	1820	1.05	100	12600
17	14	40.6	9.7	96	48	10700	13.1	1820	1.03	100	13500

[a] M, macromonomer **3**; I, initiator (MTS); solvent, THF; catalyst, TBAF ($[I]_0/[Cat]_0=1020$); temp, 50°C. [b] Determined by GPC. [c] BuOZO was polymerized using MeOTs as an initiator in CH_3CN by heating at 80°C for 24 h. [d] $[TASF]_0/[I]_0=1.23$; temp, −78°C; time, 24 h.

using TASF as catalyst in amounts of more than equimolar with MTS by reference to the coupling reaction of living poly(methyl methacrylate) performed by Sogah.[10] Though the polymers of MA-PMeOZO-14 were examined for coupling reactions in CH_3CN using respective TASF and KHF_2 as the catalysts at −78°C, no coupling product was detected.

As shown in Table III, to a solution of poly(MA-PBuOZO-*n*)s (**4**) given from MA-PBuOZO-3 and -14, BMB was added *in situ* under argon in the presence of TASF and stirred for 24 h. Products with nearly twice M_n of the feed polymers **4** were obtained in the conversion of 94 and 96%, showing formation of the coupled polymers (**5**) and living nature of **4** (Figure 3 (a)).

For mutual termination (Table IV), **1** (R = Bu; $n=13$; $M_n=1820$) was prepared by polymerization of BuOZO using MeOTs as an initiator in CH_3CN. This polymerization solution was added *in situ* to polymerization solutions of poly(MA-PBuOZO-*n*)s **4** provided from MA-PBuOZO-3 and -14 in the presence of TASF and stirred for 24 h.

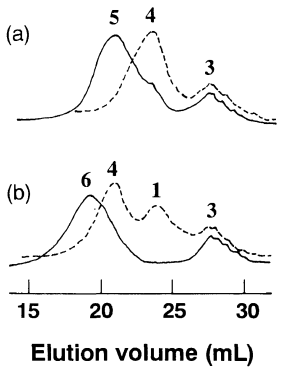


Figure 3. GPC curves of termination products of living poly(MA-PBuOZO-3) (4). (a) Entry 14: termination with BMB. (b) Entry 16: termination with living PBuOZO **1** ($n=13$). ——, mixture after termination; ------, feed mixture.

In GPC of reaction products (Figure 3 (b)), only peaks of coupling products and residual macromonomers in GTP were observed and living polymer peaks were not

detected. M_n of the products (**6**) (12600 and 13500) were reasonably higher than those (8200 and 10700) of **4**, showing formation of block copolymers. Previously, living PROZO was end-capped by terminating the propagating species (2-oxazolinium salts) with various nucleophiles to give end-functionalized polymers, *i.e.*, telechelic polymers.[2,13] It is of interest that the living ends of PROZO can be terminated by propagating species of GTP of the MA-PROZO macromonomers. The block copolymers produced by coupling reaction possess a characteristic structure of a multi-branched moiety and linear chain.

CONCLUSIONS

GTP of MA-PROZO macromonomers (**3**; MA-PROZO-*n*) by MTS as the initiator using TBAF (for MA-PBuOZO-*n*) and KHF_2 (for MA-PMeOZO-*n*) as catalysts, produced poly (MA-PROZO-*n*)s **4** with M_n up to 37600. Molecular weight distribution of **4** from **3** of $n \geq 14$ was fairly narrow, *i.e.*, $M_w/M_n = 1.08$—1.12. Rate of GTP decreased with increase in n and concentration of macromonomers, the reverse of that of radical polymerization. Maximum conversion of each macromonomers was obtained at relatively lower concentration of **3**, generally 89—95%. Poly(MA-PBuOZO-*n*)s **4** were reacted *in situ* with BMB and propagating species of living PBuOZO to provide chain extended poly(macromonomer)s (**5**) or block copolymers (**6**). The reactivity of macromonomers **3** and poly(macromonomer)s **4** and narrow molecular weight distribution of **4** indicated the living nature of present polymerization.

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