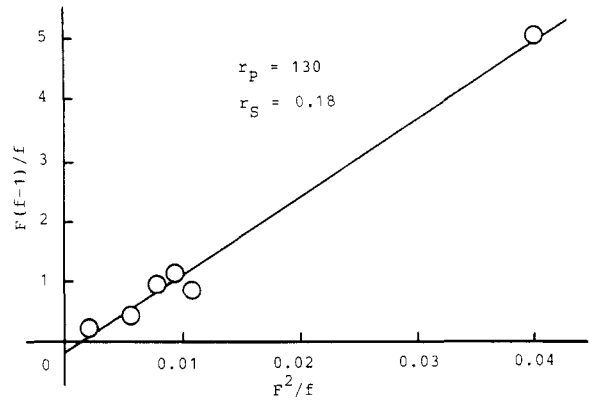

Figure 7. Fineman–Ross plots for propylene–styrene copolymerization.

Table II
Evaluation of $F(f-1)/f$ and F^2/f

run no.	F (C_P/C_S)	f (P/S)	$F(f-1)/f$	F^2/f
1	0.207	21.7	0.197	0.00197
2	0.432	34.7	0.420	0.00538
3	0.726	54.6	0.713	0.00965
4	0.863	70.4	0.854	0.0106
5	1.73	249	1.72	0.0102
6	5.18	666	5.10	0.0402

and r_S ($=k_{SS}/k_{SP}$), can be obtained by using the following Fineman–Ross equation:[12]

$$F(f-1)/f = (F^2/f)r_P - r_S \quad (6)$$

where F and f are represented by

$$F = C_P/C_S$$

$$f = \frac{\text{moles of propylene in copolymer}}{\text{moles of styrene in copolymer}}$$

where C_P is the concentration of propylene in heptane and C_S is the concentration of styrene in heptane. The results obtained are summarized in Table II and Figure 7, which gave $r_P = 130$ and $r_S = 0.18$.

Although the present catalyst system is heterogeneous, the active species are considered to be uniform in the isospecificity. (There are multiple active species that differ in the propagation rate constant, resulting in broadening the polydispersity.[4]) Therefore, the results may be as reliable as the monomer reactivity ratios over the highly isospecific catalytic centers.

In conclusion, the catalyst composed of Solvay type $TiCl_3$ and Cp_2TiMe_2 was found to be effective for the production of copolymer between propylene and styrene.

Registry No. Cp_2TiMe_2, 1271-66-5; $TiCl_3$, 7705-07-9; propylene, 115-07-1; styrene, 100-42-5; (propylene)(styrene) (copolymer), 32555-67-2.

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Synthesis of Acryl- and Methacryl-Type Macromonomers and Telechelics by Utilizing Living Polymerization of 2-Oxazolines

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ABSTRACT: Acryl- and methacryl-type macromonomers and telechelics of poly(2-alkyl-2-oxazolines) (PROZO) have been prepared for the first time by terminating the living ends in the electrophilic (cationic) ring-opening polymerization of 2-alkyl-2-oxazolines (ROZO) with suitable reagents. The synthesis of macromonomers was achieved via the following two methods: (1) by the reaction of acryloyl or methacryloyl chloride with a PROZO alcohol obtained by the hydrolysis of the living PROZO propagating species under basic conditions (indirect method) and (2) by the termination of the living species with carboxylate anions of acrylic or methacrylic acids or with trimethylsilyl methacrylate (direct method). The production of telechelics of PROZO was achieved by using a bis(2-oxazolinium salt) initiator. Termination of both living ends of the PROZO with water, ammonia, or an alkylamine afforded the corresponding telechelics of PROZO as glycols and diamines in good yields.

Introduction

Chemical modification of polymer ends is an important topic in the field of polymer synthesis because these functionalized, end-reactive polymers can be used as prepolymers for the production of various materials. In electrophilic (cationic) polymerization,[1] one of the most effective methods for the introduction of functional groups onto polymer ends is the termination of living propagating

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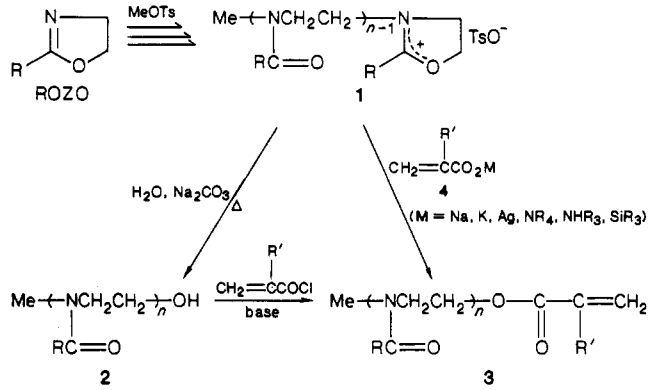
species with nucleophiles. It has been established that the cationic ring-opening polymerization of 2-alkyl-2-oxazoline (ROZO)[2] proceeds via oxazolinium species, which can easily be terminated by various nucleophiles. So far, there have been reported few syntheses of functionalized polyROZO (PROZO) using the living polymerization system of ROZO; only two preparations, poly(2-phenyl-2-oxazoline) macromonomers having a styryl group[3] and poly(2-phenyl-2-oxazoline) macromonomers of an acrylamide group,[4] are cited. It is also to be noted that styryl-type macromonomers of poly(2-oxazolines) were obtained by inducing the polymerization of 2-oxazoline monomers with vinylbenzyl halides as initiator.[4,5]

The present paper describes the first synthesis of acryl- and methacryl-type macromonomers and telechelics of PROZO utilizing the living polymerization system obtained by cationic ring-opening polymerization of ROZO, where nucleophiles like water, ammonia, an amine, and a carboxylate anion were employed as terminators.[6]

Results and Discussion

I. Synthesis of Macromonomers. Acryl-type macromonomers have been synthesized by two methods. The first involves the termination of the living propagating species of PROZO with excess water in the presence of Na_2CO_3 and the successive acylation of the resulting PROZO alcohol with acryloyl or methacryloyl chloride in the presence of a base (indirect method). The second is the introduction of acryloyl or methacryloyl groups onto the polymer ends by termination of the propagating oxazolinium species with nucleophiles such as a metal salt or a tetraalkylammonium salt of acrylic acid or methacrylic acid or a trialkylammonium salt (from a mixture of the acid and a base) or trimethylsilyl ester of methacrylic acid (direct method).



Synthesis of Acryl- and Methacryl-Type Macromonomers from PROZO Alcohols (Indirect Method). A monomer ROZO (R = Me, Et, or *n*-Bu) has been polymerized with methyl *p*-toluenesulfonate (MeOTs) as initiator in acetonitrile at 80 °C for 20 h to give PROZO 1 having a living oxazolinium species. Then the resulting polymerization solution was treated with an excess of water in the presence of Na_2CO_3 at room temperature for 30 min to hydrolyze the living species 1, giving rise to PROZO alcohol 2. However, the IR spectrum of the isolated polymer 2 showed the coexistence of a considerable amount of an ester amine type product 5. It was therefore necessary to convert 5 to 2 completely; both the hydrolysis of 1 and conversion of 5 to 2 were successively achieved by heating the reaction mixture of 1 in the presence of water and Na_2CO_3 at 100 °C for 18 h. The complete conversion was confirmed by the absence of the IR absorption due to the ester carbonyl group of 5; the structure of the product polymer is amide alcohol 2 exclusively.

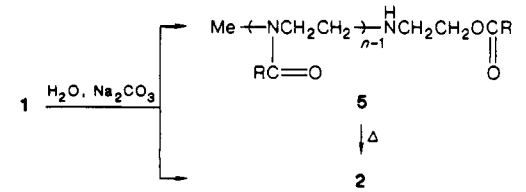
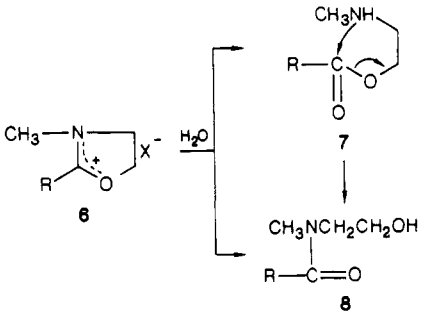


Table I
Synthesis of Acryl- and Methacryl-Type Macromonomers 3 from PROZO Alcohols 2[a]

entry	R of ROZO	M_n[b] of 2	R′	yield,[c] %	M_n[d]	n	M_w/M_n[d]
1	Me	1860	H	62	1900	21.3	1.14
2	Me	1860	Me	81	2010	22.4	1.40
3	Et	550	H	90	580	5.0	1.29
4	Et	1960	H	91	2110	20.4	1.37
5	Et	550	Me	92	590	4.9	1.15
6	Et	1960	Me	84	2180	21.1	1.32
7	*n*-Bu	3400	H	72	3530	27.1	1.35
8	*n*-Bu	3400	Me	82	3430	26.2	1.41

[a] All reactions were carried out in CH_2Cl_2 at room temperature for 24 h by using 2.0 equiv of acryloyl or methacryloyl chloride and of 2.4 equiv of Et_3N toward the alcohol 2. [b] Determined by ^1H NMR spectroscopy calculated from the signal ratio of methyl or methylene protons in the R group to the terminal *N*-methyl protons. [c] Isolated yield. [d] Determined by GPC.

Concerning the hydrolysis of an oxazolinium salt 6, the hydrolysis product of ester amine 7 is first formed as a kinetic product, which was explained by a stereoelectronic theory of the structure of hydrolysis intermediates, whereas amide alcohol 8 is formed as a thermodynamic product.[7]



In the hydrolysis of polymer analogues, therefore, the initially formed kinetic product 5 was completely isomerized to the thermodynamically more stable product 2 by heating the reaction mixture for a longer time (18 h) at 100 °C. The ^1H NMR spectra of the products showed the absence of hydrolized product of 5, amino alcohol. This fact is explained by assuming the predominant intramolecular nucleophilic attack of the amino group to the ester over hydrolysis under the conditions by using a small amount of water in acetonitrile. The chain length (n) of 2 could be readily controlled by the feed ratio $[ROZO]_0/[MeOTs]_0$ of the polymerization.

The acylation of the PROZO alcohol 2 was carried out by reacting acryloyl or methacryloyl chloride in the presence of triethylamine in dichloromethane at room temperature to give macromonomers 3 (Table I). The ^1H NMR spectroscopic analysis indicates that the functionality, i.e., the number of acryl or methacryl end groups per molecule of product macromonomers 3, is nearly unity (F = ~1.00) as determined by comparing the peak area of the methylene protons adjacent to the oxygen atom of the ester group and the vinyl protons of the acryl or methacryl group; the conversion of the alcohol 2 to the macromonomer 3 is quantitative. The decreased isolated yield of 3, however, is due to loss during the reprecipitation procedure. Gel permeation chromatographic (GPC) analysis

Table II
Synthesis of Acryl- and Methacryl-Type Macromonomers 3 by Direct Termination

	polymerizatn[a]		terminatn[b]					macromonomer 3				
entry	R of ROZO	$[ROZO]_0/[MeOTs]_0$	M	R′	solvent	temp. °C	time, h	yield, %	M_n[c]	n	M_w/M_n	F[d]
9	Me	5.2	Na	H	CH_3CN	60	30	81	570	6.1	1.34	0.56
10	Me	5.2	Na	Me	CH_3CN	60	30	80	590	6.1	1.28	0.71
11	Me	5.2	K	H	CH_3CN	60	30	78	580	6.1	1.39	0.60
12	Me	5.2	K	Me	CH_3CN	60	30	76	590	6.0	1.31	0.72
13	Me	5.2	Ag	H	CH_3CN	60	20	68	590	6.0	1.23	0.89
14	Me	5.2	Ag	Me	CH_3CN	60	6	79	610	6.0	1.19	0.99
15	Me	24.3	Ag	H	CH_3CN	60	20	70	2280	25.9	1.36	0.90
16	Me	24.3	Ag	Me	CH_3CN	60	10	75	2310	26.0	1.32	0.98
17	Et	6.5	Ag	Me	CH_3CN	60	48	67	780	7.6	1.26	0.66
18	n-Pr	6.6	Ag	Me	CH_3CN	60	48	72	940	7.7	1.41	0.58
19	Me	5.2	NMe_4	H	DMF	rt	72	60	550	6.0	1.37	0.36
20	Me	5.2	NMe_4	H	DMA	rt	72	57	530	5.8	1.45	0.36
21	Me	5.2	NMe_4	H	CH_3CN	60	12	59	550	5.8	1.40	0.52
22	Me	5.2	NMe_4	Me	DMF	rt	96	64	580	6.0	1.36	0.61
23	Me	5.2	NMe_4	Me	DMA	rt	96	52	560	6.1	1.29	0.31
24	Me	5.2	NMe_4	Me	CH_3CN	60	6	61	600	6.0	1.25	0.86
25	Me	6.6	$NHEt_3$[e]	H	CH_3CN	80	15	100	740	7.6	1.20	0.96
26	Et	5.6	$NHEt_3$[f]	H	CH_3CN	80	15	84	720	6.4	1.19	0.95
27	n-Bu	4.7	$NHEt_3$[g]	H	CH_3CN	80	15	88	760	5.8	1.35	0.82
28	n-Bu	4.5	$NHEt_3$[h]	H	CH_3CN	80	15	73	700	4.9	1.34	0.91
29	n-Bu	4.4	$NHEt_3$[i]	H	CH_3CN	80	15	78	760	5.3	1.44	0.88
30	n-Bu	4.7	$NHEt_3$[j]	Me	CH_3CN	80	15	79	520	3.3	1.21	0.95
31	n-Bu	5.8	NHPy[k]	H	CH_3CN	80	15	97	950	8.8	1.32	0.30
32	Me	5.2	$SiMe_3$	Me	CH_3CN	60	96	72	560	6.0	1.36	0.42
33	Et	6.5	$SiMe_3$	Me	CH_3CN	60	96	69	820	7.6	1.42	0.60
34	n-Pr	6.6	$SiMe_3$	Me	CH_3CN	60	96	78	930	7.7	1.38	0.55

[a] MeOTs initiator in CH_3CN at 80 °C for 20 h. [b] Carried out with a initial mole ratio 4/1 = 2.0; rt = room temperature. [c] Determined by GPC. [d] Functionality: the number of acrylate or methacrylate groups per molecule. [e] Acrylic acid/triethylamine = 0.73. [f] Acrylic acid/triethylamine = 0.60. [g] Acrylic acid/triethylamine = 0.48. [h] Acrylic acid/triethylamine = 1.0. [i] Acrylic acid/triethylamine = 2.3. [j] Methacrylic acid/triethylamine = 2.4. [k] Acrylic acid/pyridine = 0.81.

Table III
Synthesis of PROZO Glycols 12

	polymerizatn[a]				hydrolysis[b]		PROZO glycol 12		
entry	y	R	$[ROZO]_0/[10]_0$	M_n[c] of 11	11, mmol	H_2O, mL	yield, %	M_n[c]	$p+q$
35	8	Me	14.3	1910	1.45	0.6	95	1480	13.7
36	8	Me	21.3	2480	2.02	1.1	94	2080	20.7
37	8	Me	34.4	3600	1.04	0.9	92	3150	33.3
38	8	Me	46.9	4660	1.12	1.3	97	4200	45.6
39	4	Me	13.9	1830	2.02	0.8	92	1400	13.4
40	4	Me	35.8	3690	0.84	0.8	96	3240	35.0
41	8	Et	12.0	1960	1.50	0.5	91	1570	12.6
42	8	Et	24.9	3280	0.73	0.5	96	2850	25.6
43	8	n-Pr	12.0	1980	2.24	0.7	90	1600	11.3
44	8	n-Pr	25.1	3520	0.82	0.6	95	3060	24.2

[a] Bis(oxazolinium) 10 initiator in CH_3CN at 80 °C for 25 h. [b] Carried out by adding water and Na_2CO_3 to the polymerization solution and keeping the solution at 100 °C for 24 h. [c] Determined by VPO.

shows the narrow molecular weight distribution (M_w/M_n = 1.14–1.41) of **3**. Macromonomers having PMeOZO chain are soluble in water as well as common organic solvents like dichloromethane, chloroform, acetonitrile, and *N,N*-dimethylformamide (DMF), whereas other macromonomers (R = Et, *n*-Bu) were soluble in common organic solvents such as dichloromethane, chloroform, acetonitrile, and DMF.

Synthesis of Acryl- and Methacryl-Type Macromonomers via Direct Termination (Direct Method). Acryl and methacryl macromonomers **3** have also been prepared by the direct nucleophilic attack of carboxylate anion or trimethylsilyl methacrylate **4** onto the living propagating species of PROZO **1**. In the reaction using the acid salt as terminator, the solution was stirred with molecular sieves for 24 h to remove any water before use. To the solution thus prepared was added the solution of living PROZO **1**. The mixture was then allowed to react under the reaction conditions shown in Table II. The reaction mixture, using a sodium, potassium, silver, or tetramethylammonium salt in acetonitrile, was heterogeneous in appearance. It has been observed, however, that a small portion of these salts is dissolved in acetonitrile and hence the termination probably proceeds between **1** and the dissolved salt to give macromonomer **3**. On the other hand, the reaction of tetramethylammonium salt was homogeneous in DMF and *N,N*-dimethylacetamide (DMA). Nucleophilic species for termination were also generated from a mixture of acrylic or methacrylic acid and a base such as triethylamine and pyridine. The termination reaction of these systems proceeded homogeneously in acetonitrile. In the case of the trimethylsilyl ester, the system was homogeneous throughout the reaction.

In all polymerization runs the chain length (n) of **3** was controlled by the $[ROZO]_0/[MeOTs]_0$ ratio.

Among the termination reactions examined, the silver salts (entries 13–16) and tetramethylammonium methacrylate (entry 24) were very effective as terminators in terms of producing macromonomers **3** (R = Me) with high functionality and in good yields. The mixed system of

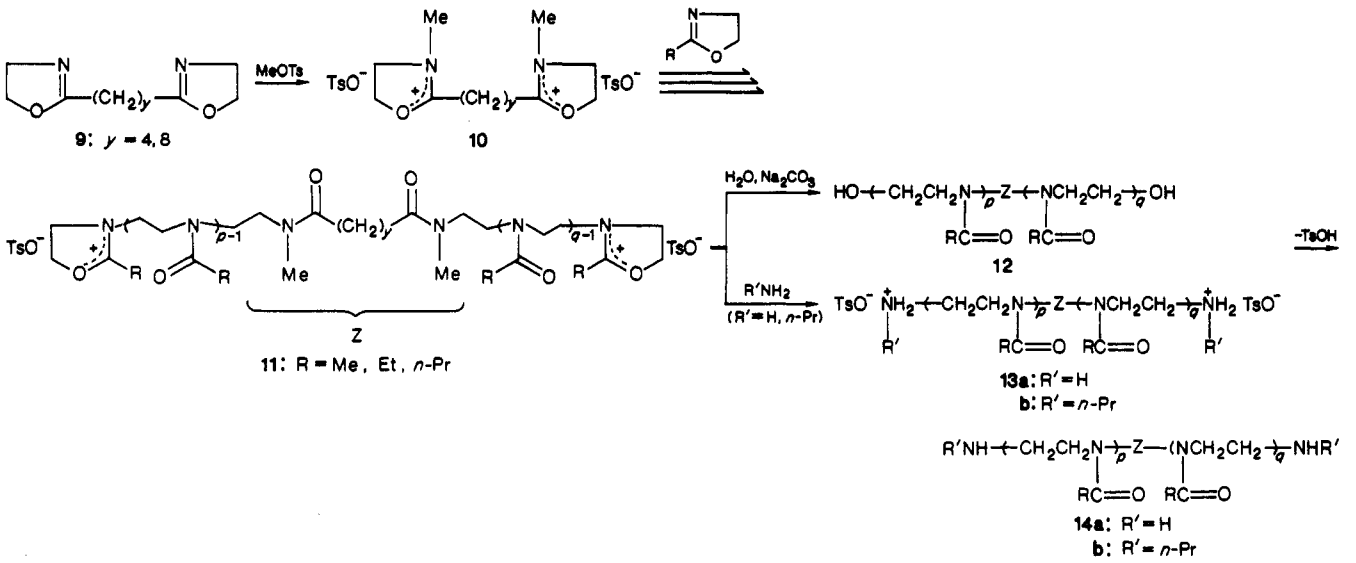


Table IV
Synthesis of PROZO Diamines 14

	polymerizatn[a]				aminatn[b]		PROZO diamine 14			
entry	y	R	$[ROZO]_0/[10]_0$	M_n[c] of 11	11, mmol	NH_3 or n-$PrNH_2$, mmol	struct	yield, %	M_n[c]	$p + q$
45	8	Me	9.8	1610	0.36	0.75	**14a**	88	1210	10.5
46	8	Me	21.3	2480	0.24	0.52	**14a**	92	2160	21.7
47	8	Me	34.4	3600	0.42	0.85	**14a**	91	3230	34.3
48	4	Me	13.9	1830	0.30	0.62	**14a**	86	1340	12.7
49	8	Et	22.1	2970	0.62	1.29	**14a**	87	2580	22.9
50	8	n-Pr	20.4	3170	0.40	0.84	**14a**	88	2720	21.3
51	8	Me	11.3	1750	0.41	0.84	**14b**	89	1430	12.1
52	8	Me	21.3	2680	0.56	1.16	**14b**	84	2350	22.9
53	8	Me	34.4	3900	0.31	0.62	**14b**	94	3550	37.0
54	4	Me	13.9	1920	0.35	0.71	**14b**	93	1570	14.4

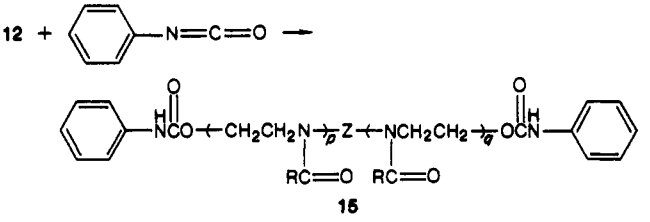
[a] Bis(oxazolinium) **10** initiator in CH_3CN at 80 °C for 25 h. [b] The ammonia or n-propylamine solution in CH_3CN was added to the polymerization solution and stirred for 30 min at 0 °C. [c] Determined by VPO.

acrylic (or methacrylic) acid and triethylamine also gave an efficient terminator. The efficiency as terminator in terms of high functionality and yield is substantially the same even when the ratio acrylic acid/triethylamine is varied as 0.48, 1.0, and 2.3 (entries 27–29). In these cases, triethylammonium acrylate is probably a nucleophilic species. The mixed system of acrylic acid/pyridine, however, produced macromonomers **3** of lower functionality in a lower yield. Sodium and potassium salts and the trimethylsilyl ester were less effective. The termination with the trimethylsilyl ester probably proceeded via the attack of tosylate anion of the propagating species on the trimethylsilyl group followed by the nucleophilic attack of methacrylate on the oxazolinium species of **1**.

II. Synthesis of Telechelics. A bis(2-oxazoline) **9** is reacted with MeOTs, giving rise to a bis(2-oxazolinium tosylate) **10**. The PROZO **11**, having living propagating species at both ends, has been prepared by polymerizing ROZO with **10** as initiator. Telechelics of PROZO, glycol **12**, and diamine **14** have been synthesized by terminating the living species **11** with water, ammonia, or n-propylamine.

Living PROZO **11** was prepared in quantitative yield by heating a mixture of ROZO and bis(2-oxazolinium salt) **10** at 80 °C for 25 h with the feed ratio $[ROZO]_0/[10]_0$ varying from 9.8 to 46.9.

The hydrolysis of PROZO living species **11** to PROZO glycol **12** has been accomplished by treating **11** with water in the presence of Na_2CO_3 at 100 °C for 24 h, similar to the procedures from **1** to **2** (Table III). The product telechelic **12** was then converted to the corresponding bis(urethane) **15** by reacting with phenyl isocyanate for determination of functionality. From ^1H NMR analysis,



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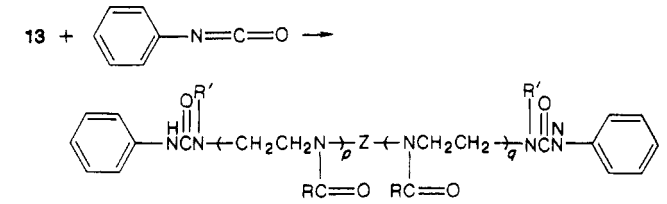
by comparing the signal intensity of phenyl protons and of N-methyl protons, the functionality of all products **15** was shown to be excellent; i.e., the hydroxyl group content per molecule was ≥1.94. The molecular weight was determined by VPO for PROZO samples **11** and **12**, before and after hydrolysis, respectively. The observed difference in molecular weight between **11** and **12** was 300–500 for all runs. This difference is close to that of the calculated value of 308 (2 × TsO − 2 × OH) within experimental error and supports the structures **11** and **12**.

The degree of polymerization, $p + q$ value, was also close to the feed ratio of ROZO and **10**, indicating living polymerization with a fast initiation with **10** followed by the relatively slow propagation of ROZO monomer.

Next, PROZO diamines **14** have been synthesized by adding an acetonitrile solution of ammonia or n-propylamine dropwise to the polymerization solution of living PROZO **11** at 0 °C. The resulting oily products of PROZO

bis(ammonium salt) **13** were characterized by ^1H NMR spectroscopy. Free diamines **14** were obtained by treating the acetonitrile solution of **13** with anhydrous K_2CO_3 (Table IV). The complete elimination of *p*-toluenesulfonic acid (TsOH) from **13** was confirmed by the absence of signals due to CN^+H_2R and to $^-O_3SC_6H_4C$ in the ^1H NMR spectra of the isolated product **14**. These telechelic diamines **14** could be successfully converted to the corresponding bis(urea) **16**, which showed the quantitative amination at both polymer ends from ^1H NMR analysis of **16**; i.e., the amino group functionality per molecule was ≥1.94.



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The molecular weight change due to the conversion from **11** to **14** was satisfactory in all runs (entries 45–54). The $p + q$ value in **14** was again very close to the $[ROZO]_0/[\mathbf{10}]_0$ ratio. All the results confirm the structures of **14a** and **14b**.

Experimental Section

Materials. Solvents, CH_3CN, CH_2Cl_2, DMF, DMA, and Et_3N, were purified by distillation over CaH_2. Et_2O was distilled over sodium wire. Commercial reagents MeOZO, EtOZO, MeOTs, *n*-$PrNH_2$, PhNCO, and pyridine were purified by distillation. Acrylic and methacrylic acids were distilled in vacuo in the presence of a radical inhibitor, *p*-methoxyphenol. Monomers *n*-PrOZO, *n*-BuOZO, and 2,2′-tetra- and octamethylenebis(2-oxazoline) **9** were prepared according to the literature.[8] Acryloyl chloride, methacryloyl chloride, hexamethyldisilazane, and tetramethylammonium hydroxide were used without purification. Sodium or potassium salts of acrylic and methacrylic acid were prepared by treating the corresponding acid with an aqueous NaOH or KOH solution and were recrystallized from water. Silver salts of acrylic and methacrylic acids were prepared from the corresponding potassium salts and silver nitrate. The tetramethylammonium salts were prepared by adding a methanol solution of tetramethylammonium hydroxide to a methanol solution of acrylic acid or methacrylic acid. The product was precipitated by adding Et_2O, isolated, and dried. Trimethylsilyl methacrylate was prepared according to the literature by using methacrylic acid and hexamethyldisilazane.[9] An acetonitrile solution of NH_3 was prepared by bubbling NH_3 gas into CH_3CN, dried over anhydrous Na_2SO_4, and titrated with an HCl solution (0.1 N), using methyl orange as an indicator. An acetonitrile solution of *n*-$PrNH_2$ was dried over molecular sieves (3A) and titrated in a similar manner. *N,N*′-Dimethyl-2,2′-tetra- or *N,N*′-dimethyl-2,2′-octamethylenebis(oxazolinium tosylate) **10** was prepared according to the literature.[2f] The solid product (y = 8) was precipitated four times from a mixed solvent of CH_3CN/Et_2O.

Measurements. ^1H NMR spectra were recorded on a JEOL JNM FX60Q FT NMR spectrometer at 23 °C with tetramethylsilane as standard. IR spectra were taken in a SHIMADZU IR-27G or JASCO IR-810 IR spectrophotometer. Molecular weight data were obtained with polystyrene standard by using a TOYO SODA HLC-802UR liquid chromatograph with TOYO SODA TSK-GEL columns, a SHIMADZU LC-3A liquid chromatograph with JASCO FINE PACK GEL 101 column, or a Corona 117 vapor pressure osmometer at 40 °C using $CHCl_3$ as eluent.

Preparation of PROZO Alcohols 2. A typical procedure for the preparation of PROZO alcohol **2** is given as follows. To a solution of MeOZO (6.85 g, 80.5 mmol) in CH_3CN (8.0 mL) was added MeOTs (0.749 g, 4.02 mmol) in CH_3CN (4.0 mL) at 0 °C under argon atmosphere and the reaction mixture was heated at 80 °C for 20 h. The resulting polymer solution was refluxed with 2.0 mL of water in the presence of Na_2CO_3 (4.46 g, 44 mmol) for 18 h. After the solvent (water–CH_3CN) was evaporated in vacuo, the residue was extracted with $CHCl_3$ (40 mL) at room temperature for 12 h. After removal of insoluble materials by filtration, $CHCl_3$ was evaporated to dryness to give 7.51 g of PMeOZO alcohol **2** (92% yield). ^1H NMR δ ($CDCl_3$) 2.1 (s, $CH_3C{=}O$), 3.0 (s, CH_3N), 3.4 (s, CH_2N); IR 1630 cm^{-1} (s, $\nu_{C=O}$, amide).

PEtOZO and PBuOZO alcohols **2** were synthesized in a similar manner except that the reaction mixture was extracted with CH_2Cl_2 (10 mL × 3) without evaporating water and CH_3CN. PEtOZO alcohol: ^1H NMR ($CDCl_3$) δ 1.1 (br, CH_3C), 2.1–2.7 (br, $CH_2C{=}O$), 3.0 (s, CH_3N), 3.5 (s, CH_2N); IR 1630 cm^{-1} (s, $\nu_{C=O}$, amide). PBuOZO alcohol: ^1H NMR ($CDCl_3$) δ 0.9 (br, CH_3C), 1.1–1.9 (br, CCH_2CH_2C), 2.0–2.6 (br, $CH_2C{=}O$), 3.0 (s, CH_3N), 3.4 (s, CH_2N); IR 1630 cm^{-1} (s, $\nu_{C=O}$, amide).

Acylation of PROZO Alcohol 2 to Macromonomer 3. The general procedure for the acylation of **2** to **3** was as follows. To a solution of PROZO alcohol **2** and Et_3N (2.4 equiv) in CH_2Cl_2 (10 mL) was added a CH_2Cl_2 solution of acryloyl chloride or methacryloyl chloride (2 equiv) and the mixture was stirred at room temperature for 24 h. A saturated Na_2CO_3 aqueous solution was added and unreacted acid chloride was decomposed by stirring the suspension for 4–8 h. For the preparation of MeOZO macromonomers, the aqueous layer was separated and evaporated to dryness. The residue was extracted with $CHCl_3$ by stirring for 12 h. After filtration of solid materials, $CHCl_3$ was evaporated to give the macromonomer. The acryl macromonomer of PMeOZO **3** (R = Me, R′ = H): ^1H NMR ($CDCl_3$) δ 2.1 (s, $CH_3C{=}O$), 3.0 (s, CH_3N), 3.4 (s, CH_2N), 4.0–4.4 (br, $CH_2OC{=}O$), 5.7–6.4 (br, $CH_2{=}CHC{=}O$); IR 1630 (s, $\nu_{C=O}$, amide), 1720 cm^{-1} (m, $\nu_{C=O}$, ester). The methacryl macromonomer of PMeOZO **3** (R = R′ = Me): ^1H NMR ($CDCl_3$) δ 1.9 (s, $CH_3C{=}C$), 3.0 (s, CH_3N), 3.4 (s, CH_2N), 4.0–4.4 (br, $CH_2OC{=}O$), 5.6 (s, $CH_2{=}CC{=}O$), 6.1 (s, $CH_2{=}CC{=}O$); IR 1630 (s, $\nu_{C=O}$, amide), 1710 cm^{-1} (m, $\nu_{C=O}$, ester).

For the preparation of macromonomers of PEtOZO and PBuOZO, the aqueous solution was extracted by CH_2Cl_2 (10 mL × 3) and the organic layer was dried over anhydrous Na_2SO_4. After filtration, the solvent was removed to give the macromonomer. The acryl macromonomer of PEtOZO **3** (R = Et, R′ = H): ^1H NMR ($CDCl_3$) δ 1.1 (br, CH_3C), 2.0–2.6 (br, $CH_2C{=}O$), 3.0 (s, CH_3N), 3.4 (s, CH_2N), 4.1–4.4 (br, $CH_2OC{=}O$), 5.8–6.5 (br, $CH_2{=}CHC{=}O$); IR 1630 (s, $\nu_{C=O}$, amide), 1720 cm^{-1} (m, $\nu_{C=O}$, ester). The methacryl macromonomer of PEtOZO **3** (R = Et, R′ = Me): ^1H NMR ($CDCl_3$) δ 1.1 (br, CH_3C), 1.9 (s, $CH_3C{=}C$), 2.0–2.6 (br, $CH_2C{=}O$), 3.0 (s, CH_3N), 3.4 (s, CH_2N), 4.0–4.4 (br, $CH_2OC{=}O$), 5.6 (s, $CH_2{=}CC{=}O$), 6.0 (s, $CH_2{=}CC{=}O$); IR 1630 (s, $\nu_{C=O}$, amide), 1720 cm^{-1} (m, $\nu_{C=O}$, ester). The acryl macromonomer of PBuOZO **3** (R = *n*-Bu, R′ = H): ^1H NMR ($CDCl_3$) δ 0.9 (br, CH_3C), 1.1–1.9 (br, CCH_2CH_2C), 2.0–2.5 (br, $CH_2C{=}O$), 3.0 (s, CH_3N), 3.4 (s, CH_2N), 4.0–4.4 (br, $CH_2OC{=}O$), 5.7–6.4 (br, $CH_2{=}CHC{=}O$); IR 1630 (s, $\nu_{C=O}$, amide), 1720 cm^{-1} (m, $\nu_{C=O}$, ester). The methacryl macromonomer of PBuOZO **3** (R = *n*-Bu, R′ = Me): ^1H NMR ($CDCl_3$) δ 0.9 (br, CH_3C), 1.1–1.8 (br, CCH_2CH_2C), 1.9 (s, $CH_3C{=}C$), 2.0–2.6 (br, $CH_2C{=}O$), 3.0 (s, CH_3N), 3.4 (s, CH_2N), 4.0–4.4 (br, $CH_2OC{=}O$), 5.6 (s, $CH_2{=}CC{=}O$), 6.0 (s, $CH_2{=}CC{=}O$); IR 1630 (s, $\nu_{C=O}$, amide), 1710 cm^{-1} (m, $\nu_{C=O}$, ester).

Termination of Living PMeOZO with Silver Methacrylate. Under nitrogen, a mixture of silver methacrylate (0.180 g, 0.93 mmol) and molecular sieves (3A, 3.00 g) in CH_3CN (3.0 mL) was stirred in the dark at room temperature for 24 h. To this mixture was added the living polymer solution containing **1** (0.258 g, 0.43 mmol) (R = Me; M_n = 600; n = 4.9) and the resulting mixture was heated at 60 °C for 6 h. Brown solids were filtered off and the filtrate was concentrated to ca. 1 mL in vacuo. Then 10 mL of CH_2Cl_2 was added and a trace amount of insoluble powder was removed by filtration. After the filtrate was concentrated to 3 mL, the residue was precipitated from Et_2O to give 0.175 g (79% yield) of macromonomer **3** (R = R′ = Me). The GPC analysis showed M_n value of 610 with M_w/M_n = 1.19. The ^1H NMR and IR spectra of the product showed similar patterns as macromonomers obtained by the indirect method. Anal. Calcd for $C_{29.03}H_{50.02}O_{8.01}N_{6.00}S_{0.05}$: C, 57.01; H, 8.24; N, 13.74; S, 0.05 (functionality F = 0.99). Found: C, 57.26; H, 8.08; N, 13.51; S, 0.00. The termination reaction using silver acrylate was carried

out in a similar manner to give the corresponding acryl macromonomers **3** (R = Me, R′ = H).

Termination of Living PMeOZO with Tetramethylammonium Methacrylate. A mixture of tetramethylammonium methacrylate (0.100 g, 0.63 mmol) and molecular sieves (4A, 3.00 g) in DMF (4.0 mL) was stirred under nitrogen at room temperature for 24 h. To this solution was added the polymer solution containing 0.186 g (0.31 mmol) of living PMeOZO **1** (R = Me; M_n = 600; n = 4.9). The mixture was stirred at room temperature for 96 h and molecular sieves were removed by filtration. To the filtrate was added 50 mL of Et_2O and the resulting polymer products were collected by filtration and dissolved in 10 mL of CH_2Cl_2. The clear solution was concentrated to 3 mL in vacuo and the residue was reprecipitated from Et_2O to give 0.109 g (64% yield) of macromonomer.

Termination of Living PBuOZO 1 (R = *n*-Bu) with Acrylic Acid in the Presence of Triethylamine. A mixture of *n*-BuOZO (0.633 g, 4.98 mmol) and MeOTs (0.208 g, 1.12 mmol) in CH_3CN (3.0 mL) was heated under argon at 80 °C for 24 h. After cooling to 0 °C, acrylic acid (0.119 g, 9.65 mmol) and Et_3N (0.167 g, 1.65 mmol) were added in this order to the solution, and the mixture was heated at 80 °C for 15 h. The mixture was cooled to room temperature and the solvent was evaporated in vacuo. The residue was dissolved in 20 mL of $CHCl_3$ and washed twice with a 1 N $NaHCO_3$ aqueous solution. The organic layer was dried over anhydrous Na_2SO_4 and the solvent was evaporated in vacuo to dryness giving macromonomer **3** (R = *n*-Bu; M_n = 700; 0.519 g; 73% yield).

Termination of living PEtOZO **1** (R = Et) with acrylic acid in the presence of Et_3N was similarly carried out to give macromonomer **3** (R = Et; M_n = 720) in 84% yield.

Termination of Living PMeOZO 1 (R = Me) with Acrylic Acid in the Presence of Triethylamine. A mixture of MeOZO (0.560 g, 6.58 mmol) and MeOTs (0.186 g, 1.00 mmol) in CH_3CN (3.0 mL) was heated under argon at 80 °C for 24 h. After cooling to 0 °C, acrylic acid (0.103 g, 1.43 mmol) and Et_3N (2.00 g, 1.95 mmol) were added in this order to the solution, and then the mixture was heated at 80 °C for 15 h. The mixture was cooled to room temperature and the solvent was evaporated in vacuo. The residue was dissolved in 20 mL of $CHCl_3$ and extracted with a 1 N $NaHCO_3$ aqueous solution. The aqueous layer was evaporated in vacuo to dryness and the residue was extracted with $CHCl_3$ by stirring the mixture for 6 h. After filtration of solid materials, $CHCl_3$ was evaporated to give the macromonomer **3** (0.577 g, quantitative).

Termination of Living PBuOZO 1 (R = *n*-Bu) with Acrylic Acid in the Presence of Pyridine. A mixture of *n*-BuOZO (0.66 g, 5.79 mmol) and MeOTs (0.186 g, 1.00 mmol) in CH_3CN (3.0 mL) was heated under argon at 80 °C for 24 h. After cooling to 0 °C, acrylic acid (0.151 g, 2.10 mmol) and pyridine (0.200 g, 2.58 mmol) were added in this order to the solution, and the mixture was heated at 80 °C for 20 h. The mixture was cooled to room temperature and the solvent was evaporated in vacuo. The residue was dissolved in 20 mL of $CHCl_3$ and washed twice with a 1 N $NaHCO_3$ aqueous solution. The organic layer was dried over anhydrous Na_2SO_4 and the solvent was evaporated in vacuo to dryness giving macromonomer **3** (R = *n*-Bu; M_n = 950; 0.709 g; 97% yield; F = 0.30).

Termination of Living PMeOZO 1 (R = Me) with Trimethylsilyl Methacrylate. To an CH_3CN (3 mL) solution of trimethylsilyl methacrylate (0.194 g, 1.23 mmol) was added the living polymer solution containing 0.354 g (0.59 mmol) of PMeOZO **1** and the reaction mixture was stirred at 60 °C for 96 h under nitrogen. To the mixture, cooled to room temperature, 30 mL of Et_2O was added to precipitate polymeric materials. Then the polymers were dissolved in CH_3CN reprecipitated from Et_2O and dried in vacuo to give 0.24 g (72% yield) of white solid macromonomer **3** (M_n = 560 and M_w/M_n = 1.36 by GPC analysis): ^{1}H NMR (CD_3CN) δ 2.0 (s, CH_3C=O), 2.3 (s, CH_3Ar), 3.0 (s, CH_3N), 2.9–3.9 (s, CH_2N), 4.2 (br, CH_2OC=O) 5.6 (s, CH_2=CC=O), 6.1 (s, CH_2=CC=O), 7.4, 7.6 ($MeC_6H_4SO_3$); IR 1640 (s, $\nu_{C=O}$, amide), 1720 cm^{-1} (m, $\nu_{C=O}$, ester). From the ratio of signals at 4.2 and 2.0, the functionality of **3** was obtained as 42%. The content of tosylate anion was calculated as 61% by comparing the CH_3N protons and aromatic protons. Anal. Calcd for $C_{30.74}H_{51.16}O_{8.58}N_{6.00}S_{0.58}$: C, 55.88; H, 7.81; N, 12.72; S, 2.81 (functionality F = 0.42). Found: C, 56.09; H, 7.71; N, 12.97; S, 2.63.

Synthesis of Glycol 12 by the Hydrolysis of Living Bis(oxazolinium ions) of PMeOZO 11. To a polymerization solution containing 2.77 g (1.45 mmol) of living PMeOZ **11** (R = Me; y = 8) prepared by the polymerization of MeOZO with initiator **10** was added water (0.6 mL) and anhydrous Na_2CO_3 (13.2 mmol). The resulting suspension was stirred at 100 °C for 24 h. After the solvent was evaporated the residue was extracted twice with 10 mL of $CHCl_3$ and the organic layer was dried over anhydrous Na_2SO_4. The solution was concentrated in vacuo to ca. 3 mL and Et_2O (30 mL) was added to precipitate polymeric materials, which were isolated and dried to give 2.20 g of white powdery materials of PMeOZO glycol **12** (95% yield). VPO analysis of **12** (R = Me) gave M_n = 1480 and $p + q$ = 13.7: ^{1}H NMR ($CDCl_3$) δ 1.3 (br, NC(=O)$CH_2(CH_2)_6CH_2$C(=O)N), 2.1–2.5 (br, NC(=O)$CH_2(CH_2)_6CH_2$C(=O)N), 2.1 (s, CH_3C=O), 3.0 (s, CH_3N), 2.7–3.9 (br, CH_2N). Anal. Calcd for $C_{70.8}H_{127.9}O_{17.7}N_{15.7}$: C, 57.37; H, 8.70; N, 14.83. Found: C, 57.15; H, 8.82; N, 15.09.

Preparation of Bis(urethane) 15. The glycol **12** thus obtained (0.157 g, 0.11 mmol) was dissolved in 2.0 mL of CH_3CN and treated with phenyl isocyanate (0.027 g, 0.23 mmol) at 0 °C under a nitrogen atmosphere. The mixture was stirred at 60 °C for 3 h followed by refluxing for 1 h. Precipitation from CH_3CN/Et_2O gave the corresponding bis(urethane) **15** as a white powdery material, 0.171 g (94% yield): ^{1}H NMR (CD_3CN) δ 1.3 (br, NC(=O)$CH_2(CH_2)_6CH_2$C(=O)N), 2.1–2.5 (br, NC(=O)-$CH_2(CH_2)_6CH_2$C(=O)N), 2.0 (s, CH_3C=O), 3.0 (s, CH_3N), 2.7–3.9 (br, CH_2N), 4.2 (br, CH_2OC(=O)N), 6.8–7.7 (m, OC(=O)NC_6H_5), 8.9 (s, OC(=O)NHPh); IR 3130 (w, ν_{NH}, urethane), 1730 (m, $\nu_{C=O}$, urethane), 1640 cm^{-1} (s, $\nu_{C=O}$, amide). The introduction of phenyl groups at both PMeOZO chain ends obtained from the peak ratio of aromatic protons and CH_3N protons was quantitative (F = 2.0). Anal. Calcd for $C_{84.4}H_{137.9}O_{19.7}N_{17.7}$: C, 59.20; H, 8.08; N, 14.41. Found: C, 59.43; H, 8.23; N, 14.64.

Synthesis of Diamine 14a by the Ammoniolysis of Living Bis(oxazolinium ions) of PMeOZO 11. To a methanol (15 mL) solution of living PROZO **11** (0.580 g, 0.36 mmol) was added a CH_3CN solution of NH_3 (0.74 mmol) at 0 °C under a nitrogen atmosphere and the solution was stirred for 30 min to form a white suspension. By addition of Et_2O to this suspension bis(ammonium salt), **13a** (R = Me) was obtained, after evaporation of the solvent, as a viscous oily product, 0.580 g (98% yield): ^{1}H NMR (CD_3CN) δ 1.2 (br, NC(=O)$CH_2(CH_2)_6CH_2$C(=O)N), 2.1–2.5 (br, NC(=O)$CH_2(CH_2)_6CH_2$C(=O)N, 2.0 (s, CH_3C=O), 2.3 (s, $ArCH_3$), 2.9 (s, CH_3N), 2.7–4.1 (br, CH_2N), 5.1 (br, CNH_3^+), and 7.2, 7.6 ($^-O_3SC_6H_4C$).

To a CH_3CN (10 mL) solution of **13a** (R = Me) was added anhydrous K_2CO_3 (5.0 g) and the suspension was stirred at room temperature for 48 h. The insolubles were filtered off and the filtrate was poured into Et_2O giving white powdery **14a** (R = Me) (0.356 g, 90% yield) after complete drying: ^{1}H NMR (CD_3CN) δ 1.3 (br, NC(=O)$CH_2(CH_2)_6CH_2$C(=O)N), 2.1–2.5 (br, NC(=O)$CH_2(CH_2)_6CH_2$C(=O)N), 2.0 (s, CH_3C=O), 3.0 (s, CH_3N), 2.6–3.7 (br, CH_2N). Anal. Calcd for $C_{58}H_{107.5}O_{12.5}N_{14.5}$: C, 57.66; H, 8.97; N, 16.81. Found: C, 57.43; H, 8.85; N, 17.08.

Preparation of Bis(urea) 16. Under nitrogen, the product diamine **14a** (R = Me) (0.182 g, 0.15 mmol) and phenyl isocyanate (0.038 g, 0.32 mmol) was dissolved in CH_3CN (2.5 mL) and the solution was stirred at 0 °C for 2 h and at room temperature for 2 h. The resulting solution was poured into Et_2O to precipitate the product which was reprecipitated from CH_3CN/Et_2O to give bis(urea) **16** (R = Me, R′ = H), a white powdery material, 0.25 g (95% yield) after drying: ^{1}H NMR (CD_3CN) δ 1.3 (br, NC(=O)$CH_2(CH_2)_6CH_2$C(=O)N), 2.1–2.5 (br, NC(=O)$CH_2(CH_2)_6C$-H_2C(=O)N, 2.0 (s, CH_3C=O), 3.0 (s, CH_3N), 2.7–4.0 (br, CH_2N), 6.1 (s, PhNHC(=O)N). The functionality of this polymer was determined to be almost 2.0 by the comparison of phenyl protons and CH_3N protons in the ^{1}H NMR spectroscopy. Anal. Calcd for $C_{72}H_{117.5}O_{14.5}N_{16.5}$: C, 59.79; H, 8.19; N, 15.98. Found: C, 59.92; H, 8.30; N, 16.21.

Conclusion

The present study provides several functionalized poly(*N*-acylethylenimine) chains of poly(2-alkyl-2-oxazolines) (PROZOs), acryl and methacryl macromonomers of

PROZO, and glycol and diamine type telechelics of PROZO. These functionalized PROZOs have been prepared by using the living cationic polymerization of 2-alkyl-2-oxazolines (ROZOs). The macromonomers were obtained via the hydrolysis of living PROZO ends followed by the esterification of the product PROZO alcohol[10] (indirect method) and via the direct nucleophilic attack of acrylate or methacrylate onto living PROZO ends (direct method). Glycol and diamine telechelics of PROZO were produced via the hydrolysis and the ammoniolysis or aminolysis of living PROZO ends initiated with a bis(2-oxazolinium salt). These functionalized PROZOs have various potentials for application. For example, present macromonomers can be copolymerized by a radical initiator with various vinyl monomers to give copolymers having PROZO graft chains which are useful as a surface modifier or a polymeric surfactant,[11] and the telechelic glycols and diamines are employed as prepolymers for the production of a polyurethane and polyurea, respectively.[6c] Furthermore, the present synthetic method will readily lead to more highly functionalized PROZOs, e.g., block type macromonomers with surfactant natures.[12]

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(10) Preparation of a product PROZO amine followed by the amidation with acryloyl or methacryloyl chloride to an acryl or methacryl amide type macromonomer of PROZO will be published elsewhere.

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