End Capping of Growing Species of Poly(2-oxazoline) with Carboxylic Acid: A Novel and Convenient Route To Prepare Vinyl- and Carboxy-Terminated Macromonomers

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ABSTRACT: This paper describes a new methodology of end-capping esterification of the growing oxazolinium end group of the polymerization of 2-oxazolines (2-methyl and 2-ethyl derivatives), which is accomplished by the binary system of carboxylic acid and a proton scavenger of hindered base such as 2,6-lutidine. Reaction conditions for complete and quantitative end capping have been established. The new methodology has successfully been applied to the synthesis of macromonomers having an acrylate end group (end capping with acrylic acid) and having a carboxylic acid end group (end capping with a dibasic acid). In addition, an A–B–A type block copolymer between poly[(*N*-acylimino)ethylene] and poly(oxyethylene) was readily prepared by using poly(oxyethylene) dicarboxylic acid (PEO acid).

Introduction

Ring-opening polymerization of 2-oxazolines (1) proceeds without transfer and termination under appropriate reaction conditions. It has also been known that the growing end of the oxazolinium salt structure readily reacts with amines and with water to yield ring-opened products, quantitatively. These results had been combined to prepare the end-functionalized 2-oxazoline polymers, i.e., macromonomers, and telechelic polymers.[1,2]

The reaction of oxazolinium salt with carboxylate anion is expected to proceed smoothly since the same reaction is the key step of the propagation of "no catalyst copolymerization" between cyclic imino ethers and acrylic acid.[3,4] However, as far as we examined, it was very difficult to realize the quantitative reaction of the oxazolinium salt with carboxylate anion. The difficulty may be due to the poor solubility of carboxylate salt in aprotic polar solvents, which are suitable for the polymerization of 2-oxazolines. Moreover, it was also not always easy to remove the unreacted carboxylate salt from the product of end-functional polymer.

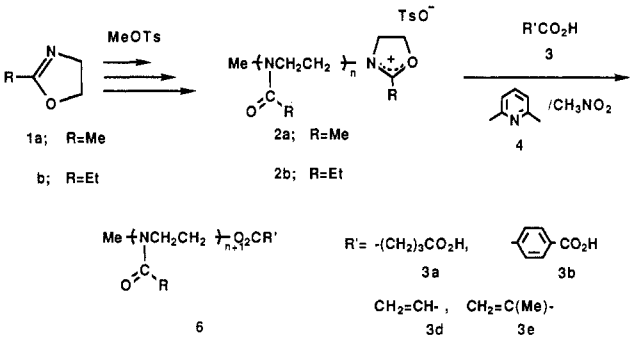
The present paper describes a new methodology of the ester end capping of the oxazolinium growing end of the 2-oxazoline polymers, poly[(*N*-acylimino)ethylenes] (2), by the reaction with a carboxylic acid in the presence of a proton scavenger such as 2,6-lutidine (4), which reacts with proton but not with the oxazolinium ring. End-capping reactions with acrylic acid (also methacrylic acid) and with a dibasic acid gave rise to the production of macromonomers with the acrylate (also methacrylate) terminal group and with carboxylic acid terminal group (Scheme I).

Experimental Section

Materials. 2,3-Dimethyl-2-oxazolinium tosylate (5), a model of the oxazolinium growing end, was prepared according to a previous paper.[5] A bifunctional initiator, 1,4-bis(3-methyl-2-oxazolinium-2-yl) hexyl ditriflate (7), was prepared by a previously reported procedure.[6] PEO acid no. 4000 (M_n, 3220; F_n (degree of functionalization per molecule), 1.96) (3c) was supplied from Kawaken Fine Chemical Co. (Japan) and was purified by reprecipitation from hexane. Glutaric acid was purified by recrystallization from chloroform. Terephthalic acid was used without further purification. The other reagents and all the solvents were commercial and were purified by repeated distillation under nitrogen.

Measurements. ^{1}H NMR and IR spectra were recorded respectively on a 60-MHz Hitachi R-600 NMR spectrometer and Hitachi 260-20 infrared spectrometer. Molecular weight determination was carried out on a vapor pressure osmometer, a Hitachi Model 117 in $CHCl_3$ at 40 °C. GPC analysis was performed by using TSK-GEL G2500H or G4000H columns in DMF containing 0.4% triethylamine at 50 °C.

Scheme I



General Procedure of Polymerization Followed by End-Capping Esterification. In a glass tube equipped with a magnetic stirrer and a three-way stopcock were mixed 6.23 g (73.2 mmol) of **1a** and 0.147 g (0.789 mmol) of methyl tosylate in 20 mL of nitromethane under cooling with ice. The tube was kept at 70 °C for 45 h for polymerization. Then, a small portion (3 mL) of the reaction mixture was poured into 15 mL of diethyl ether to precipitate a polymeric product, which was isolated and purified further by repeated reprecipitation from methanol (solvent) to diethyl ether (precipitant). After drying in vacuo, white solid polymer was obtained. The isolated polymer yield was calculated at 98%.

The remaining reaction mixture was transferred by a syringe to another tube equipped with a magnetic stirrer and a three-way stopcock, in which were placed 2.00 g (15.8 mmol) of **3a**, 7.0 mL (47 mmol) of **4**, and 7 mL of nitromethane. The tube was kept at 70 °C for 19 h. Then, the reaction mixture was poured into 200 mL of diethyl ether to precipitate the polymeric product, which was dissolved in 100 mL of methanol and treated with 0.4 g (1.7 mequiv) of Amberlyst 15 at room temperature for 3 h with stirring. After the filtration, the filtrate was poured again into 300 mL of diethyl ether to precipitate the product, which was purified further by repeated reprecipitation from methanol to diethyl ether. After drying in vacuo, pale yellow solid polymer was obtained. The polymer yield was 83%. The number-average molecular weight of the resulting polymer measured by GPC was found to be 11 200.

The analysis of the end group (carboxylic acid) of the above polymer was performed by titration in aqueous solution with 0.01 N aqueous NaOH. The degree of functionalization was calculated to be 1.09 on the basis of the combination of molecular weight and end group analysis.

Results and Discussion

Model Reaction. It has been known that sterically hindered base, e.g., 2,6-lutidine (4), is less nucleophilic than

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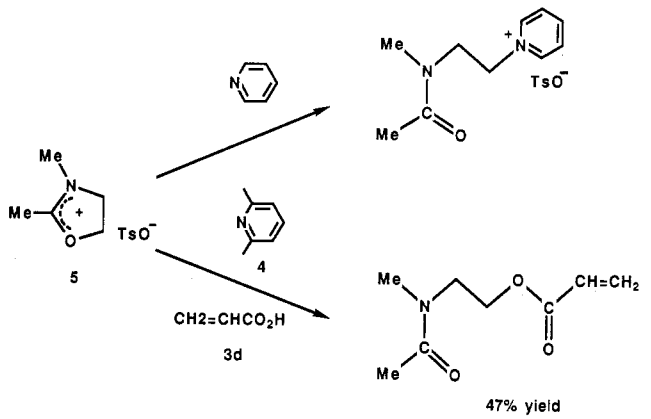
Table I
Polymerization of 2-Oxazolines (2-Methyl and 2-Ethyl Derivatives) Followed by End-Capping Esterification

	polymerization[a]					end-capping esterification					end-capped polymer			
run no.	1	[M]/[I]	solvent	temp, °C	time, h	3	[3]/[I]	[4]/[I]	temp, °C	time, h	yield, %	$\bar{M}_n$[b]	$\bar{M}_w/\bar{M}_n$[b]	$\bar{F}_n$[c]
1	**1a**	12	CH_3CN	70	25	**3a**	10	20	50	12	82	1070[d]		0.95
2	**1a**	21	CH_3CN	70	48	**3a**	9.4	19	50	12	61	1880	1.16	1.03
3	**1a**	36	DMF	80	36	**3a**	20	42	100	29	62	3920	1.31	0.96
4	**1a**	92	CH_3NO_2	70	45	**3a**	23	68	70	19	83	11200	1.16	1.09
5	**1a**	107	CH_3NO_2	70	44	**3a**	23	68	70	19	82	10600	1.16	1.06
6	**1a**	11	CH_3CN	80	15	**3b**	10	25	50	15	82	1400[d]		0.68
7	**1b**	34	CH_3NO_2	70	44	**3a**	20	60	70	18	90	6560	1.22	1.16
8	**1b**	50	CH_3NO_2	70	44	**3a**	20	60	70	18	98	9300	1.20	1.09
9	**1b**	98	CH_3NO_2	70	44	**3a**	19	57	70	56	85	12000	1.09	1.08
10[e]	**1a**	22	CH_3NO_2	70	33	**3a**	22	65	70	60	95	2400	1.25	1.96
11	**1a**	19	CH_3NO_2	70	20	**3c**	0.38	0.72	80	70	71	7800	1.17	1.99[f]

[a] Methyl tosylate was used as initiator [I]. [b] Determined by GPC measurement. Each of the calibration curves was obtained by using standard samples of **3a** and **3b** described in the text. [c] Average of degree of functionalization per molecule. [d] Determined from the integral ratio in the ^1H NMR spectra. [e] **7** was used as initiator. [f] Average number of poly[(*N*-acetylimino)ethylene] block in one molecule of block copolymer.

Scheme II



pyridine.[7] In the present paper, **4** was used as a proton scavenger in the reaction of the oxazolinium salt with carboxylic acid.

2,3-Dimethyl-2-oxazolinium salt **5**, a model compound of the growing end of **2**, was ring-opened by a common base (a 2 M amount) such as pyridine to produce the corresponding pyridinium salt (Scheme II). The extent of conversion of **5** was followed by ^1H NMR spectroscopy of the reaction mixture. The conversion of **5** at 35 °C was 41% after 35 min and almost complete after 17 h. On the contrary, the reaction between **5** and **4** did not occur even after 20 h under similar reaction conditions. When acrylic acid was present in the latter system, **4** acted as a base to scavenge proton, the ring-opening reaction of **5** with carboxylate anion occurred, and *N*-methyl-*N*-(2-acryloloxy)-ethylacetamide was isolated in a moderate yield as the sole product after purification by column chromatography. On the contrary, in the absence of **4** no reaction between **5** and the acid took place under similar conditions.

Carboxylic Acid Terminated Poly[(*N*-acylimino)-ethylene]. Poly(2-oxazoline) having the terminal carboxylic acid group was prepared when large excess amounts of a dicarboxylic acid and **4** were added to the polymerization system of **1** (Table I). One of the carboxylic acid groups of dibasic acid was used in esterification, and the other remained unreacted. 2-Methyl- (**1a**) and 2-ethyl-2-oxazolines (**1b**) were used as monomers, and glutaric acid (**3a**) was used mainly as the dibasic acid because of its high solubilities in the solvents used. The polymerization of **1** was performed with varying amounts (1–10 mol %) of methyl tosylate at 70–80 °C and went to completion after 15–48 h. Then, large excess amounts of **3** and **4** were added to the polymerization system, and the mixture was kept at 50–100 °C to complete the end-capping esterification. The end-capped polymer (**6**) was isolated by reprecipitation, which was then treated with an ion-exchange resin (Amberlyst 15) in methanol to acidify the end carboxy group and also to remove 2,6-hydrolutidinium tosylate. After several reprecipitations from methanol to diethyl ether, analytically pure **6** was obtained. The molecular weight of **6** was determined by GPC analysis by using standard samples of **2**.[8] Before GPC measurement, **6** was treated with an excess amount of dimethylformamide dimethylacetal to convert the carboxylic acid group to the corresponding methyl ester in order to avoid both the aggregation of carboxylic acid group and the interaction of the polymer with the gels in the GPC column. The accuracy of the molecular weight measurement by GPC was confirmed by comparing the values with those of standard samples determined by VPO.

Table II
Effect of Reaction Conditions on $\bar{F}_n$ Values

run[a] no.	solvent	temp, °C	time, h	yield, %	$\bar{F}_n$
3	DMF	80	43	65	0.82
3	DMF	100	43	62	0.96
4	CH_3NO_2	50	15	46	0.93
4	CH_3NO_2	50	40	47	0.95
4	CH_3NO_2	70	15	42	1.10
4	CH_3NO_2	70	40	51	0.93
4	CH_3NO_2	100	15	45	1.05

[a] The feeds and the conditions for the polymerization as well as the feeds for the end-capping esterification are the same as those in the corresponding run no. in Table I.

The analysis of the terminal carboxylic acid was conveniently performed by simple titration of aqueous polymer solution with 0.01 N aqueous NaOH. The degree of functionalization of the polymers (F_n) was calculated from the molecular weight and the amount of the terminal carboxylic acid group by titration. Complete and quantitative half-esterification with glutaric acid has been achieved, as is shown by the F_n value in Tables I and II. With terephthalic acid (**3b**), whose solubility in the reaction medium of CH_3CN is low, the F_n value is not high enough. The end capping of half-esterification was successfully carried out in acetonitrile, DMF, or nitromethane. In nitromethane, the F_n value was always close to 1.0 under varying reaction conditions (Table II). Thus, it is concluded that the oxazolinium end of **2** readily reacts with **3a**, and the resulting product is substantially stable at temperatures below 100 °C. In DMF on the other hand, the complete half-esterification requires higher temperatures. In Figure 1, the GPC chart of **6a** (run no. 3) is

Table III
Preparation of Poly[(*N*-acetylimino)ethylene] Acrylate and Methacrylate[a] Macromonomers

		end capping					end-capped polymer			
run no.	[M]/[I]	3	[3]/[I]	[2]/[I]	temp, °C	time, h	yield, %	$\bar{M}_n$[b]	$\bar{M}_w/\bar{M}_n$[b]	$\bar{F}_n$[c]
1	9.2	**3d**	17	50	70	24	44	1,310	1.27	0.70
2	18	**3d**	17	50	70	24	60	2,070	1.29	0.50
3	8.3	**3d**	26	81	70	48	80	1,120	1.10	0.94
4	16	**3d**	30	78	70	48	51	2,190	1.24	0.96
5	7.6	**3e**	30	80	70	48	62	1,020	1.18	1.06

[a] Polymerization was carried out in nitromethane at 70 °C for 24 h. [b] Determined by GPC measurement. [c] Degree of functionalization per molecule determined by ^{1}H NMR.

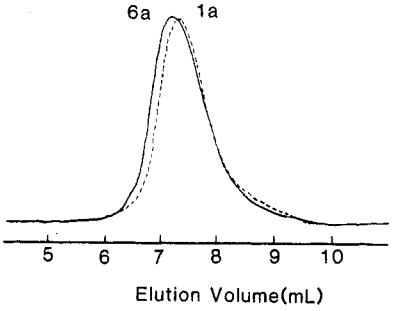
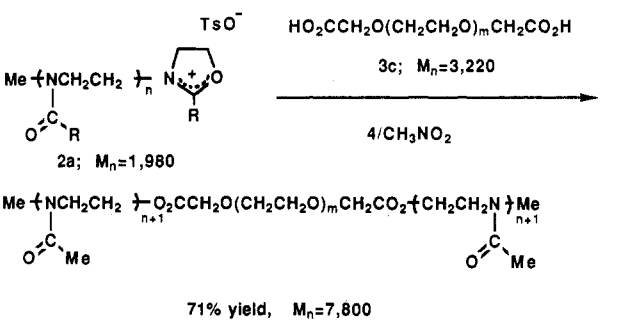


Figure 1. Gel permeation chromatograms of poly[(*N*-acetylimino)ethylenes] before (**1a**) and after ester end capping (**6a**) (run no. 3 in Table I, TSK-GEL G2500H column, DMF containing 0.4% Et_3N at 1.0 mL/min, with RI detection).

compared with that of the corresponding initial polymer without end capping. It is clearly shown that the diester polymer, whose molecular weight would be twice as high as that of the half-ester, has not been formed. In other words, only one carboxylic acid group of dibasic acid has been reacted. In run no. 10, a bifunctional initiator, 1,4-bis(3-methyl-2-oxazolinium-2-yl) hexyl ditriflate (**7**), was used in the polymerization of 2-methyl-2-oxazoline. In this case a telechelic polymer with two carboxylic acid groups at both ends of the polymer was obtained, whose F_n value was 1.96. The ester end-capping reaction was further applied to the preparation of an A–B–A type copolymer. When poly(oxyethylene) having α,ω-dicarboxylic acid groups (PEO acid, **3c**; M_n = 3220) was reacted with an excess amount of **2** with a living oxazolinium end in the presence of **4**, an A–B–A type triblock copolymer consisting of poly[(*N*-acetylimino)ethylene] (A block) and poly(oxyethylene) (B block) was prepared (Scheme III). The separation of the block copolymer from the unreacted homopolymer **2** was easily performed since the former was soluble in benzene and the latter was not. The comparison of GPC curves of **2**, **3c**, and the block copolymer clearly shows the formation of the A–B–A type block copolymer (Figure 2). The ratio between the two blocks (A and B) was estimated at 1.99 by ^{1}H NMR spectroscopy and the molecular weight of each of the A and B blocks. This value is in good agreement with the F_n value of the starting PEO acid (1.96). Thus, the A–B–A type triblock copolymer was prepared almost completely without any noticeable amount of A–B type diblock copolymer. Block copolymer with a similar structure prepared by a different method has been reported to be a powerful antielectrostatic polymeric reagent for Nylon 6 fiber.[9]

Poly[(*N*-acylimino)ethylene] Macromer with Terminal Acrylate (or Methacrylate) Group. The reaction of the growing oxazolinium end of **2** with acrylic acid was similarly performed. Large excess amounts of acrylic acid (**3d**) and of **4** were also used for complete conversion of oxazolinium end groups. In the present case, a small

Scheme III



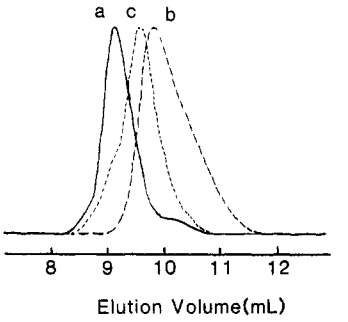


Figure 2. Gel permeation chromatograms of poly[(*N*-acetylimino)ethylene]-block-poly(oxyethylene) (a) and two starting polymers **1a** (b) and **3c** (c) (TSK-GEL G4000H column).

amount of benzoquinone was to be added to the reaction system in order to inhibit radical polymerization of the resulting macromonomer and unreacted acrylic acid. The introduction of the acrylate end group was confirmed by both ^{1}H NMR and IR spectroscopies. The peaks of vinyl protons of the acryloyl end group appeared at around δ 5.7–6.7 in ^{1}H NMR, and the peak for the C=O stretching band of conjugated ester appeared at 1720 cm^{-1} in IR. The degree of functionalization was determined by the ^{1}H NMR integral ratio between the peak of methyl protons at the initiating end and those of the vinyl group. With larger excess amounts of both acid and **4** and with a longer duration time of reaction, an F_n value close to 1.00 was achieved. Methacrylate macromer with F_n = 1.06 was prepared in the same way.

Poly[(*N*-acylimino)ethylene] macromonomers having terminal vinyl groups have previously been prepared by the end capping of the oxazolinium group at the growing end with aminoalkyl-substituted styrene and by 2-oxazoline polymerization with an initiation of *p*-(iodomethyl)-styrene[1] or 2-(*p*-styryl)-2-oxazolinium salt.[10] The method of the present study constitutes the third method and is carried out conveniently. Poly[(*N*-acylimino)ethylenes] are characterized by high hydrophilicity and high compatibility with many polymers.[11] Therefore, the end-reactive polymers of 2-oxazolines which have been prepared

in the present study are deemed promising in the so-called "molecular designing" of polymer modifications.

Registry No. (1a)(oxirane) (block copolymer), 118018-34-1; 5, 40743-18-8; *N*-methyl-*N*-(2-acryloloxy)ethylpyridium tosylate, 118018-33-0; pyridine, 110-86-1; *N*-methyl-*N*-(2-acryloloxy)-ethylacetamide, 45029-68-3; acrylic acid, 79-10-7.

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End-Group and Main-Chain Resonance Assignments for the Aliphatic Polyamide-4,6, -6,6, and -6 via Two-Dimensional NMR Methods

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ABSTRACT: The end-group and main-chain resonances in the ^1H and ^{13}C NMR spectra of a low molecular weight oligomer of polyamide-4,6 (PA-4,6) have been assigned by using various 2D NMR techniques (H–H and X–H COSY, RCT, and COLOC). Model compounds, mimicking the amine, carboxylic, and pyrrolidone end groups present in PA-4,6, were synthesized to assist in the assignments. Results have been interpolated to the observed ^{13}C chemical shifts of the end groups of high molecular weight PA-6 and -6,6, which has led to a partial assignment in these aliphatic polyamides. Main-chain resonances of PA-6 and -6,6 have been assigned unambiguously via H–H and X–H COSY measurements.

Introduction

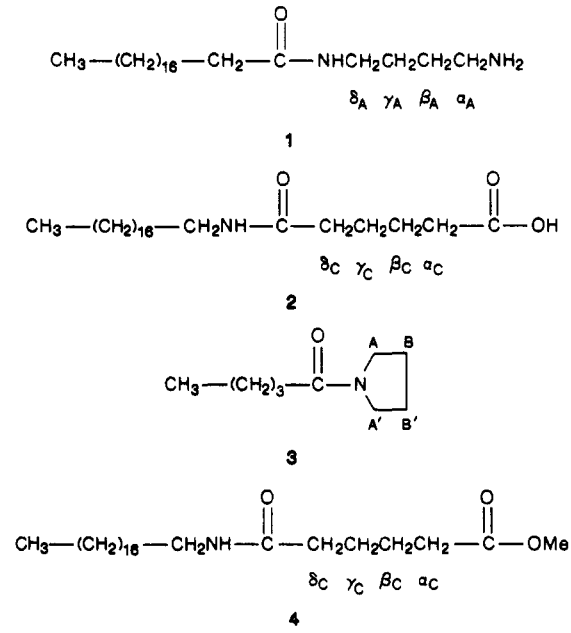
Since the pioneering work of Carothers[1] on the synthesis of homo- and copolyamides, several reports have appeared in the literature dealing with the characterization of aliphatic, mixed aliphatic–aromatic, and aromatic polyamides using ^1H, ^{13}C, or ^{15}N NMR. Both due to the intrinsic simplicity of the ^1H and ^{13}C NMR spectra of homopolyamides and the availability of other methods for the characterization of the homopolyamides (IR spectroscopy, the combination of hydrolytic cleavage techniques and thin-layer chromatography),[2,3] the majority of these publications have dealt with sequence analysis of aliphatic copolyamides and aromatic copolyamides using either ^{13}C NMR[4,5] or ^1H NMR, respectively.[6,7]

So far no unambiguous ^{13}C chemical shift assignments exist for the main-chain aliphatic carbons in the polyamides PA-6, PA-6,6, and the recently introduced polyamide-4,6 (Stanyl, trademark of DSM). Moreover, to our knowledge, hardly any or no ^1H and/or ^{13}C chemical shift data exist for the end groups, being present in the above-mentioned polyamides. The absence of these data might be due to a number of reasons: (i) the partial failure of ^{13}C chemical shift increment data in polar solvents as formic acid, fluorosulfonic acid, and sulfuric acid; (ii) the absence of model compounds mimicking the expected end groups, (iii) the unavailability of 2D NMR techniques (see, for a detailed discussion, ref 8).

In this work we have exploited at least one advantage of the recently introduced new synthesis of PA-4,6.[9] This polyamide is prepared in a two-step polymerization process, leading initially to a low molecular mass oligomer, which is subsequently postcondensed in the solid or molten state to the corresponding high molar mass PA-4,6. The number of end groups present in the oligomer and the polymer, amine (a), carboxyl (c), and pyrrolidone (p), can be determined via titration methods.[10,11]

We have extensively investigated this particular oligomer of polyamide-4,6, being the target molecule for the end-group analysis, with a variety of 2D NMR techniques (H–H COSY,[12] X–H COSY,[13] RCT,[14] and COLOC[15]).

Chart I



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