

Living Cationic Polymerization of δ -Valerolactone and Synthesis of High Molecular Weight Homopolymer and Asymmetric Telechelic and Block Copolymer

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ABSTRACT: Poly(δ -valerolactone) [poly(δ VL)] of high molecular weight ($\sim 40\,000$) and low polydispersity index (~ 1.05) was prepared by activated monomer cationic ring-opening polymerization of δ -VL initiated by the alcohol/HCl·Et₂O system. A series of functional alcohols, e.g., 9-anthracenemethanol, 2-hydroxyethyl acrylate, 3-buten-1-ol, 2-bromoethanol, and 5-norbornene-2-methanol, were successfully used to prepare asymmetric telechelic poly(δ VL), i.e., chains end-capped by the functional group of the alcohol in α -position and by an ω -hydroxyl group. Ring-opening polymerization of δ -VL in the presence of α -methoxy- ω -hydroxypoly(ethylene oxide) and poly(ethylene glycol) led to amphiphilic di- and triblock copolymers, respectively. The polydispersity index of all these (co)polymers was low (~ 1.10).

Introduction

Interest in the design, synthesis, and properties of biodegradable polymers is steadily increasing because of potential applications in biology, medicine, and pharmacy and as environmentally friendly materials. Lactones, lactides, and glycolide are among the most used monomers for the synthesis of biodegradable polymers by ring-opening polymerization (ROP) according to a variety of mechanisms, including cationic, anionic, and coordinative and based on active hydrogen or zwitterionic species.¹ The ROP of lactones is living mainly in the case of the coordinative mechanism.^{1,2} Nevertheless, the “activated monomer cationic polymerization” reported by Penczek et al.^{3–5} is an interesting alternative to suppress irreversible chain stopping reactions, such as inter- and intramolecular transesterification reactions. This method was reported to polymerize epichlorohydrin and propylene oxide into linear polymers without formation of cyclic oligomers.⁴ Okamoto⁵ reported on the ROP of β -propiolactone, δ -valerolactone (δ -VL), and ϵ -caprolactone (ϵ -CL) by a combination of an alcohol and triethyloxonium hexafluorophosphate. Polymers with controlled although low molecular weight ($M_n < 3000$) and rather high polydispersity index (~ 1.4) were formed. According to Hedrick et al.⁶ and Okada et al.,⁷ the alcohol/scandium trifluoromethanesulfonate pair is an effective initiator for ROP of lactones. Aliphatic polycarbonate ($M_n < 10\,000$) with low polydispersity index (~ 1.15) was prepared by Endo et al.⁸ by ROP of 1,3-dioxepane-2-one initiated by an alcohol/HCl·Et₂O combination. Controlled ROP of ϵ -CL and δ -VL and block copolymerization with 1,3-dioxepane-2-one were also conducted in the presence of 1-butanol/HCl·Et₂O and H₂O/HCl·Et₂O.⁹ The molecular weight distributions for these (co)polymers were narrow, and the molecular weight was rather low ($< 15\,000$ for poly(ϵ CL) and < 5000 for poly(δ VL)). This paper reports the synthesis of poly(δ VL) with high molecular weight and low polydispersity using an alcohol/HCl·Et₂O initiator.

Because the alcohol is the actual initiator, it should dictate the structure of the α end group of the chains. To confirm this expectation, primary alcohols of different structures and bearing groups with specific properties and reactivities were used as listed in Figure 1. In agreement with the mechanism proposed for the activated monomer ROP of lactones,⁸ α -functional, ω -hydroxypoly(δ -valerolactone) should be formed. In the case of poly(ethylene glycol), the polymerization should produce amphiphilic block copolymers. This strategy is actually reminiscent of the one used in ROP polymerization initiated by functional aluminum alkoxide (Et_xAl(ORX)_{3-x}) prepared by reaction of triethylaluminum (AlEt₃) with functional alcohol (X–R–OH, where X is a tertiary amine, a bromine, a polymerizable double bond, etc.).^{10–12}

Experimental Section

Materials. ϵ -Caprolactone (ϵ -CL, 99%, Aldrich), δ -valerolactone (δ -VL, Tech., Aldrich), and dichloromethane (99.6%, Aldrich) were dried over calcium hydride for 48 h at room temperature and distilled under reduced pressure just before use. A 2.0 M HCl solution in diethyl ether (Et₂O) was purchased from Aldrich and diluted by dry dichloromethane (0.1 M). 1-Butanol (99.4%, Aldrich), and 3-buten-1-ol (96%, Aldrich) were dried over calcium hydride for 48 h and distilled under reduced pressure and dissolved in dry dichloromethane (0.1 M). 9-Anthracenemethanol (97%, Aldrich), poly(ethylene glycol) ($M_n = 4600$, PEG4.6 K, Aldrich), and monomethoxypoly(ethylene glycol) ($M_n = 2000$, MPEG2K, Aldrich) were dried by azeotropic distillation of previously dried toluene (three times) just before use. 2-Bromoethanol (95%, Aldrich), 5-norbornene-2-methanol (98%, mixture of endo and exo, Aldrich), and 2-hydroxyethyl acrylate (96%, Aldrich) were dried over molecular sieves and distilled under reduced pressure and dissolved in dry dichloromethane (0.1 M).

Polymerization of δ -VL Initiated by Alcohol/HCl·Et₂O. In a typical experiment, 20 mg of 9-anthracenemethanol (0.096 mmol) was first added into a previously flamed glass reactor and dried by azeotropic distillation of toluene (three times). Then, 1.0 mL of δ -VL (11 mmol), 1.0 mL of dichloromethane, and 2.0 mL of HCl·Et₂O in dichloromethane (0.1 M) were added through a rubber septum with a syringe or a stainless capillary at 0 °C. After 2 h, the reaction mixture was poured into 100 mL of cold heptane. The precipitated polymer was

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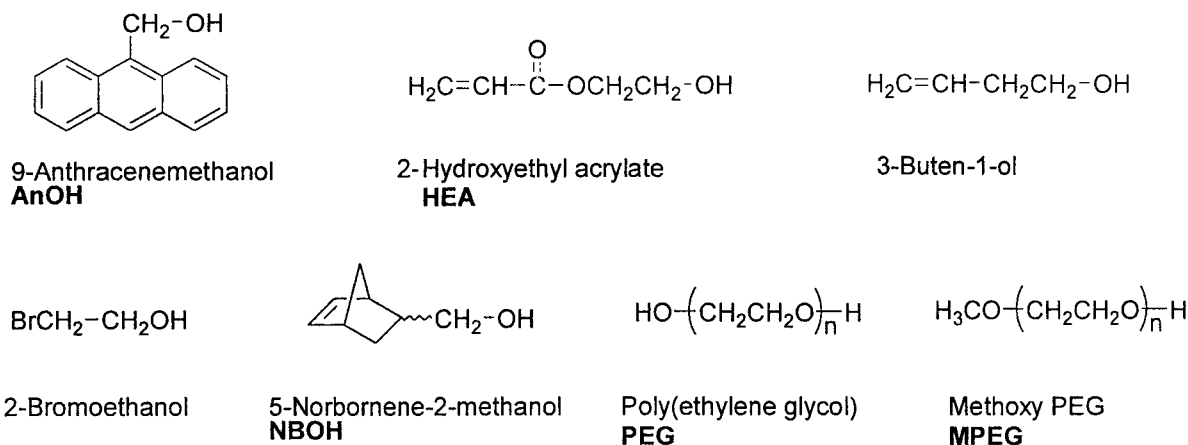


Figure 1. List of the primary alcohols used as initiators of the δ -VL polymerization by the activated monomer cationic mechanism.

recovered by filtration and dried at 25 °C for 24 h under reduced pressure (95% yield). ^1H NMR (CDCl_3): δ 8.5 (s, 0.014H, anthracene-), 8.3 (d, 0.029H, An-), 8.0 (d, 0.028H, An-), 7.4–7.6 (m, 0.056H, An-), 6.15 (s, 0.029H, An- CH_2 -), 4.1 (t, 2H, $-\text{CO}_2\text{CH}_2$ -), 3.65 (s, 0.026H, $-\text{CH}_2\text{OH}$), 2.3 (t, 2H, $-\text{CH}_2\text{CO}-$), 1.8 (m, 0.045H), and 1.6 ppm (m, 4H, $-\text{CH}_2-\text{CH}_2$ -). The degree of polymerization (DP) for poly(δ VL) was calculated from the relative intensity of the signals of 6.15 and 4.1 ppm, i.e., DP = 69 and $M_{n,\text{NMR}} = 6900$.

^1H NMR (CDCl_3) of poly(δ VL) ($M_{n,\text{NMR}} = 11\,000$) initiated by 2-hydroxyethyl acrylate/ $\text{HCl}\cdot\text{Et}_2\text{O}$: δ 6.4 (dd, 0.009H, $\text{CH}_2=\text{CH}-$), 6.1 (dd, 0.009H, $\text{CH}_2=\text{CH}-$), 5.8 (dd, 0.009H, $\text{CH}_2=\text{CH}-$), 4.3 (m, 0.044H, $-\text{CO}_2-\text{CH}_2\text{CH}_2-\text{CO}-$), 4.1 (t, 2H, $-\text{CO}_2\text{CH}_2$ -), 3.65 (s, 0.019H, $-\text{CH}_2\text{OH}$), 2.3 (t, 2H, $-\text{CH}_2\text{CO}-$), and 1.6 ppm (m, 4H, $-\text{CH}_2-\text{CH}_2$ -).

^1H NMR (CDCl_3) of poly(δ VL) ($M_{n,\text{NMR}} = 6000$) initiated by 3-buten-1-ol/ $\text{HCl}\cdot\text{Et}_2\text{O}$: δ 5.7 (m, 0.017H, $\text{CH}_2=\text{CH}-$), 5.1 (m, 0.033H, $\text{CH}_2=\text{CH}-$), 4.1 (t, 2H, $-\text{CO}_2\text{CH}_2$ -), 3.65 (s, 0.036H, $-\text{CH}_2\text{OH}$), 2.3 (t, 2H, $-\text{CH}_2\text{CO}-$), and 1.6 ppm (m, 4H, $-\text{CH}_2-\text{CH}_2$ -).

^1H NMR (CDCl_3) of poly(δ VL) ($M_{n,\text{NMR}} = 11\,000$) initiated by 2-bromoethanol/ $\text{HCl}\cdot\text{Et}_2\text{O}$: δ 4.4 (t, 0.022H, $\text{BrCH}_2-\text{CH}_2-\text{O}-$), 4.1 (t, 2H, $-\text{CO}_2\text{CH}_2$ -), 3.65 (s, 0.019H, $-\text{CH}_2\text{OH}$), 3.50 (t, 0.018H, BrCH_2 -), 2.3 (t, 2H, $-\text{CH}_2\text{CO}-$), and 1.6 ppm (m, 4H, $-\text{CH}_2-\text{CH}_2$ -).

^1H NMR (CDCl_3) of poly(δ VL) ($M_{n,\text{NMR}} = 7500$) initiated by 5-norbornene-2-methanol/ $\text{HCl}\cdot\text{Et}_2\text{O}$: δ 5.9–6.2 (t, 0.027H, $-\text{CH}=\text{CH}-$), 4.1 (t, 2H, $-\text{CO}_2\text{CH}_2$ -), 3.65 (s, 0.027H, $-\text{CH}_2\text{OH}$), 2.5–2.9 (m, 0.034H, $-\text{CH}-$), 2.3 (t, 2H, $-\text{CH}_2\text{CO}-$), 1.8–2.0 (m, 0.050H, $-\text{CH}_2$ -), 1.6 ppm (m, 4H, $-\text{CH}_2-\text{CH}_2$ -), and 0.5 ppm (m, 0.014H, $-\text{CH}_2$ -).

Synthesis of PEG-VL Block Copolymers. In a typical experiment, 0.21 g of monomethoxypoly(ethylene glycol) ($M_n = 2000$, MPEG2K) was added into a previously flamed glass reactor and dried by azeotropic distillation of toluene. Then, 2.0 mL of dichloromethane, 1.0 mL of δ -VL (11 mmol), and 1.5 mL of $\text{HCl}\cdot\text{Et}_2\text{O}$ in dichloromethane (0.1 M) were added at 0 °C. After 3 h, the reactor was opened, and 3.0 mL of dichloromethane was added; the mixture was poured into 150 mL of cold heptane. The precipitated polymer was separated by filtration and dried at 25 °C for 24 h under reduced pressure (1.2 g, 92% yield). ^1H NMR (CDCl_3): 4.3 (t, 0.025H, $-\text{OCH}_2\text{CH}_2-\text{O}-\text{CO}-$), 4.1 (t, 2H, $-\text{CO}_2\text{CH}_2$ -), 3.8 (m, 0.019H, $-\text{OCH}_2-\text{CH}_2-\text{O}-\text{CO}-$), 3.6 (s, 4.2H, $-\text{CH}_2\text{O}$), 3.40 (s, 0.038H, $\text{CH}_3\text{O}-$), 2.3 (t, 2H, $-\text{CH}_2\text{CO}-$), and 1.6 ppm (m, 4H, $-\text{CH}_2-\text{CH}_2$ -). The composition of the block copolymer was calculated from the relative intensity of the signals of the poly(δ VL) methylene protons ($\delta = 4.1$ ppm) and the MPEGM ethylene protons ($\delta = 3.6$ ppm).

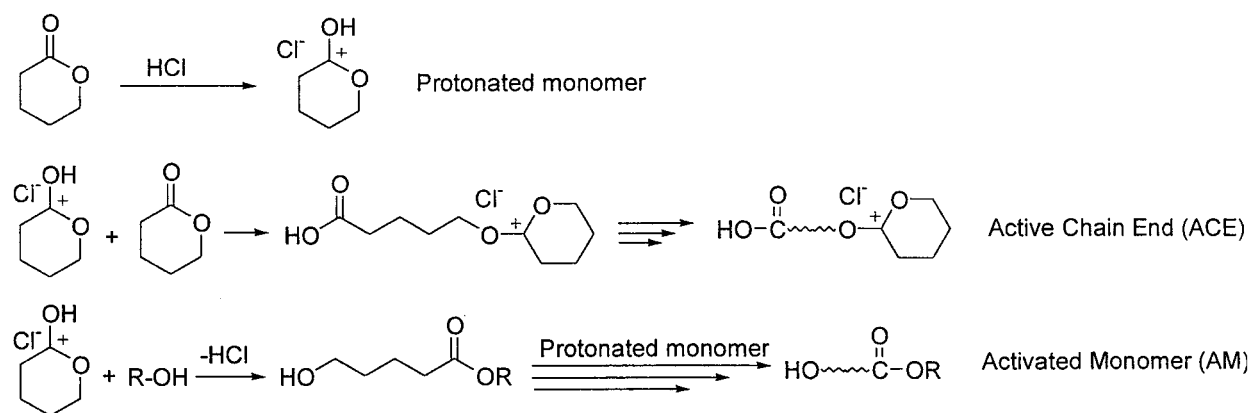
Characterization. Size exclusion chromatography (SEC) was performed in THF at a flow rate of 1.0 mL/min at 40 °C using a Hewlett-Packard 1090 liquid chromatograph equipped with a Hewlett-Packard 1037A refractive index and an ultraviolet detector. Columns (HP PL gel 5 μm ; pore sizes of 10^5 , 10^4 , 10^3 , and 100 Å) were calibrated with polystyrene stan-

dards. The viscometric relationships for polystyrene and poly(ϵ -caprolactone) in THF at 40 °C were used to build up an universal calibration curve.¹³ A ^1H NMR spectrum was recorded in CDCl_3 at 400 MHz in the FT mode with a Bruker AN 400 apparatus at 25 °C.

Results and Discussion

Synthesis of High Molecular Weight Poly(δ VL) Initiated by 1-Butanol/ $\text{HCl}\cdot\text{Et}_2\text{O}$. Endo et al. used the same initiator to synthesize poly(δ VL) with controlled molecular weight and low polydispersity index (<1.20) by the activated monomer cationic mechanism in dichloromethane.⁹ However, the chains were systematically short ($M_n \approx 3000$). According to Penczek et al.,⁴ the instantaneous monomer-to-alcohol molar ratio should be as low as possible in order to limit the contribution of the active chain end mechanism to propagation (Scheme 1), which leads to undesirable reactions, such as cyclization. For instance, epichlorohydrin was polymerized by slowly adding the monomer to the two-component initiator.⁴ In this study, δ -VL was polymerized by the 1-butanol/ $\text{HCl}\cdot\text{Et}_2\text{O}$ system at higher monomer concentration and higher monomer-to-initiator (1-butanol) molar ratio. Table 1 shows the experimental data collected in dichloromethane for different monomer-to-1-butanol molar ratios ($[\text{M}]_0/[\text{I}]_0$). Because HCl is an activator,⁹ it is not taken into account for calculating the theoretical molecular weight. At low $[\text{M}]_0/[\text{I}]_0$ (<300), the $[\text{HCl}]/[\text{alcohol}]$ ratio was fixed at 3 and the temperature at 0 °C, and the initial monomer concentration ($[\text{M}]_0$) was 4.0 M or higher (entries 1a–1c in Table 1). Polymerization was close to completion within 5 h, and the experimental molecular weight ($M_{n,\text{exp}}$) that was calculated according to the $M_{n,\text{SEC}}$ and the conversion factor F (Table 2) was consistent with a controlled polymerization process. Furthermore, the polydispersity indices were low and seemed to decrease with the monomer concentration (1a and 1c compared to 1b in Table 1). When the $[\text{M}]_0/[\text{I}]_0$ ratio was increased to 760 (entry 1d, Table 1), polymerization became slower although the HCl to initiator molar ratio was increased. The monomer conversion was 65% within 14.5 h. The $M_{n,\text{exp}}$ agrees with $M_{n,\text{th}}$ and the polydispersity index is low, despite a high molecular weight. When the polymerization was made faster by increasing the temperature to 25 °C and the $[\text{HCl}]/[\text{I}]_0$ ratio to 7, the molecular weight distribution was broader (entry 1f in Table 1), and $M_{n,\text{exp}}$ was then smaller than $M_{n,\text{th}}$, which indicates loss of control.

Scheme 1

Table 1. Ring-Opening Polymerization of δ -VL Initiated by the 1-Butanol/HCl-Et₂O System

entry	monomer	[HCl]/[I] ₀	[M] ₀ (M)	[M] ₀ /[I] ₀	temp (°C)	time (h)	yield (%)	$M_{n,th}^a \times 10^{-4}$	$M_{n,SEC} \times 10^{-4}$	$M_{n,exp}^c \times 10^{-4}$	M_w/M_n
1a	δ -VL	3.0	4.0	170	0	1.5	98	1.7	2.2	1.9	1.06
1b	δ -VL	3.0	6.5	250	0	3	95	2.4	2.4	2.1	1.15
1c	δ -VL	3.0	4.0	250	0	5	95	2.4	2.4	2.1	1.03
1d	δ -VL	3.0	4.0	760	0	14.5	65	4.9	4.3	3.7	1.02
1e	δ -VL	3.0	4.0	610	25	25	70	4.3	3.2	2.7	1.07
1f	δ -VL	7.0	4.0	610	25	24	89	5.4	3.2	2.7	1.24
1g	ϵ -CL	3.0	4.0	130	25	29	95	1.6	1.1 ^b		1.25
1h	ϵ -CL	3.0	4.0	90	25	24	95	1.0	0.7 ^b		1.16

^a Theoretical molecular weight in the case of living polymerization. ^b $M_{n,SEC}$ based on the universal calibration valid to poly(ϵ CL).¹³
^c $M_{n,exp} = M_{n,SEC}/F$, where $F = 1.17 \pm 0.15$ is the conversion factor calculated from data in Table 2.

Table 2. Ring-Opening Polymerization of δ -VL Initiated by the Alcohol/HCl-Et₂O System at 0 °C in CH₂Cl₂; Conditions: [HCl]/[I]₀ = 3.0, [M]₀ = 3.0 M

entry	initiator	[M] ₀ /[I] ₀	time (h)	yield (%)	$M_{n,th} \times 10^{-3}$	$M_{n,NMR}^b \times 10^{-3}$	$M_{n,SEC}^{a,b} \times 10^{-3}$	M_w/M_n
2a	AnOH ^c	50	2	98	5.0	6.9	7.1	1.10
2b	AnOH	114	2	95	11.4	12.0	14.1	1.08
2c	HEA ^d	91	2.5	98	9.1	11.0	13.0	1.08
2d	3-buten-1-ol	53	2	95	5.3	6.0	8.1	1.07
2e	2-bromoethanol	98	2.5	98	9.8	11.0	12.3	1.10
2f	NBOH ^e	51	2	95	5.1	7.5	8.4	1.10

^a Calibration with PS standards. ^b $M_{n,SEC}/M_{n,NMR} = 1.17 \pm 0.15$; factor for converting apparent $M_{n,SEC}$ into absolute M_n for poly(δ VL) in THF at 40 °C. ^c 9-Anthracenemethanol. ^d 2-Hydroxyethyl acrylate. ^e 5-Norbornene-2-methanol.

For comparison, ϵ -caprolactone (ϵ -CL) was substituted for δ -VL and polymerized at 25 °C by the same initiating system. Polymerization is slow (compare 1a and 1g in Table 1), and the polydispersity index is higher at higher [M]₀/[I]₀ (>100). Poly(ϵ CL) with molecular weight higher than 15 000 could not be prepared with a narrow molecular weight distribution by the 1-butanol/HCl-Et₂O system, in contrast to poly(δ VL) that could be successfully prepared with high molecular weight (40 000) and low polydispersity (~1.05).

Synthesis of Asymmetric Telechelic Poly(δ VL).

As aforementioned, the α end group of poly(δ VL) initiated by the alcohol (ROH)/HCl-Et₂O system should be the RO- group of the alcohol, such that the activated monomer cationic ROP would be an easy way to prepare a variety of end-functionalized polyesters. The primary alcohols listed in Figure 1 were used as initiators for the polymerization of δ -VL at 0 °C in dichloromethane in the presence of HCl-Et₂O used in a 3-fold molar excess with respect to the alcohol. As shown in Table 2, the polymerization was nearly quantitative within 2 h. The experimental molecular weight ($M_{n,NMR}$) agrees well with the theoretical value based on the monomer-to-initiator molar ratio and the monomer conversion, which confirms that the polymerization is controlled whatever the initiator used. The low polydispersity indices (~1.10)

indicate that initiation is faster than propagation, which is also much faster than any irreversible chain-breaking reaction. Systematic comparison of $M_{n,SEC}$ and $M_{n,NMR}$ for the six samples listed in Table 2 can be used to calculate the conversion factor (F) of the apparent $M_{n,SEC}$ based on polystyrene calibration into absolute M_n . So, the apparent $M_{n,SEC}$ data reported in Table 1 were systematically corrected by this factor F ($M_{n,exp} = M_{n,SEC}/F$). $M_{n,NMR}$ was calculated from the relative intensity of the -CH₂-OH protons (ω end-group) and the -CH₂-O- protons of the repeat units ($\delta = 4.1$ ppm).

The ¹H NMR spectrum for poly(δ VL) initiated by 9-anthracenemethanol (AnOH) is shown in Figure 2 (entry 2a in Table 2, $M_n = 6900$, $M_w/M_n = 1.10$). In addition to resonances at 1.6, 2.3, and 4.1 ppm that can be assigned to the methylene protons of the repeat unit, peaks at 7.4–8.5 (a–d) and 6.15 ppm (e) are characteristic of the protons of the anthracene end group and the methylene adjacent to it, respectively. The relative intensity of peak e (α end-group) and of the peak characteristic of the terminal -CH₂-OH confirms that there are as many α end groups that originate from the initiator as ω end groups formed by hydrolysis of the propagating species, in accordance with the activated monomer mechanism (Scheme 1). Additional resonances at 1.8 and 4.3 ppm (marked by "+") are tentatively

Table 3. Synthesis of Block Copolymers in Dichloromethane at 0 °C; Conditions: $[\text{HCl}]_0/[\text{OH}]_0 = 3.0$, $[\text{M}]_0 = 3.0 \text{ M}$

entry	macroinitiator	f_{VL} (wt %)	$[\text{M}]_0/[\text{OH}]_0$	time (h)	yield (%)	F_{VL}^a (wt %)	$M_{n,\text{th}}(\text{PVL})^b$ $\times 10^{-3}$	$M_{n,\text{NMR}}(\text{PVL})^c$ $\times 10^{-3}$	$M_{n,\text{SEC}}$ $\times 10^{-3}$	M_w/M_n
3a	MPEG(2K)	0.70	45	2	95	0.68	4.5	4.3	9.5	1.09
3b	MPEG(2K)	0.83	90	3	92	0.81	8.2	8.0	16.8	1.09
3c	PEG(4.6K)	0.70	50	2.5	98	0.68	10.0	10.8	19.0	1.07

^a Calculated by ^1H NMR. ^b Theoretical molecular weight of the poly(δ VL) block. ^c Molecular weight of the poly(δ VL) block extracted from the copolymer composition (^1H NMR) and M_n of (M)PEG.

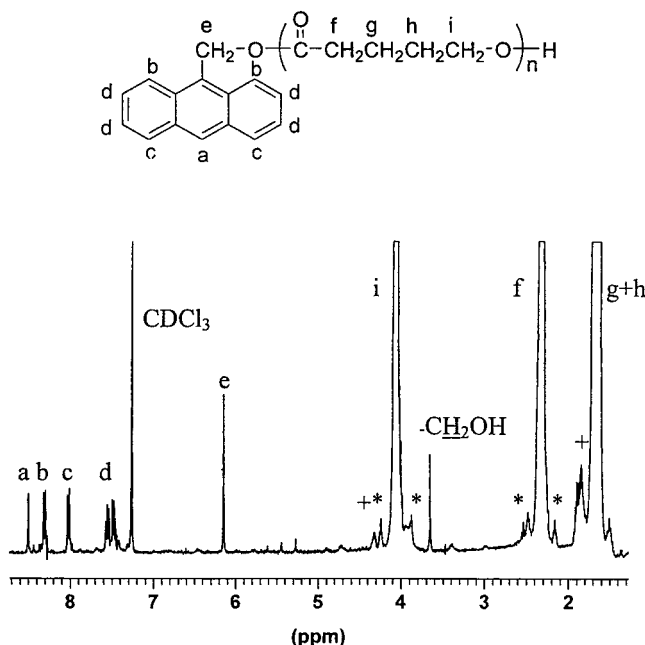


Figure 2. ^1H NMR spectrum of poly(δ VL) initiated by the 9-anthracenemethanol/ $\text{HCl}\cdot\text{Et}_2\text{O}$ system (2a; in Table 2). Signals marked by "*" refer to sidebands. Signals marked by "+" refer to cyclics.

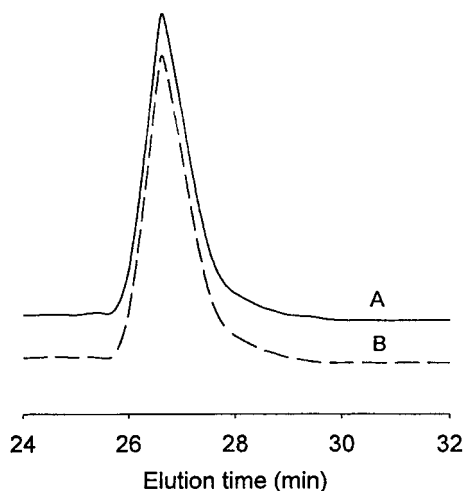


Figure 3. SEC chromatograms of poly(δ VL) initiated by the 9-anthracenemethanol/ $\text{HCl}\cdot\text{Et}_2\text{O}$ system (2b; in Table 2, $M_n = 14\,100$, $M_w/M_n = 1.08$): (A) refractive index detector; (B) UV detector (366 nm).

assigned to small amount of cyclics (<2%). Figure 3 compares the SEC traces the polymer 2b (Table 2) recorded by the dual refractive index and ultraviolet (366 nm) detector. The elution peaks are monomodal and narrow, and they can be superimposed, which confirms the quantitative end-capping of the chains by the initiator fragment. The anthracene end group is a fluorescent label useful to locate the chains in relation to their interaction with an environmental medium.¹⁴

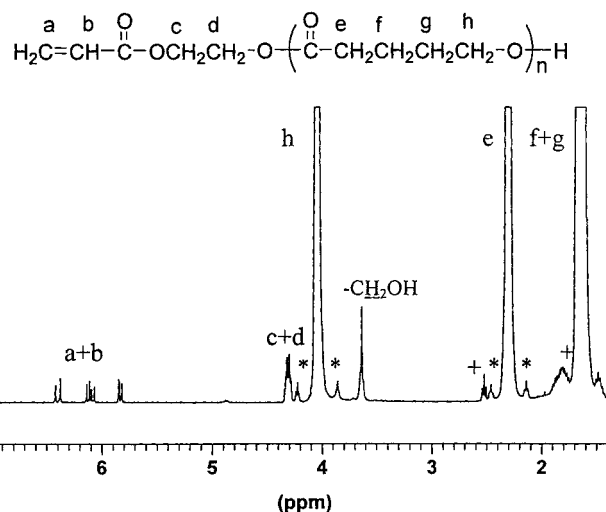


Figure 4. ^1H NMR spectrum of poly(δ VL) initiated by the 2-hydroxyethyl acrylate/ $\text{HCl}\cdot\text{Et}_2\text{O}$ system (2c; in Table 2). Signals marked by "*" refer to sidebands. Signals marked by "+" refer to cyclics.

A terminal $\text{C}=\text{C}$ double bond corresponds to a macromonomer, which can be used to produce graft copolymer.¹¹ The double bond can also be easily derivatized, e.g., by epoxidation, bromination, and hydrosilylation.¹⁵ This concept was illustrated by initiating the ring-opening polymerization of δ -VL by 2-hydroxyethyl acrylate (HEA) and 3-buten-1-ol, respectively. Peaks at 5.8–6.4 (a+b) and 4.3 ppm (c+d) in the ^1H NMR spectrum of poly(δ VL) initiated by HEA (Figure 4) can be assigned to the protons of the acrylate double bond and the ethyl of the ester group, respectively. Peaks at 5.1 and 5.7 ppm in the ^1H NMR spectrum of poly(δ VL) initiated by 3-buten-1-ol are the signature of the butenyl end group. Furthermore, molecular weight calculated from the relative intensity of peaks characteristic of the end groups and the methylene repeat units (4.1 ppm) are in accordance with the theoretical value. Clearly, the structure of the initiating alcohol does not impede the control of the δ -VL polymerization by the activated monomer mechanism.

The use of 2-bromoethanol as initiator of the cationic ROP of δ -VL leads to the same conclusion. Peaks at 3.5 and 4.4 ppm in the ^1H NMR spectrum confirm that ethyl bromide is the α end group. Derivatization of this end group by quaternization and nucleophilic substitution is an easy way to increase the range of end-functionalized poly(δ -VL).^{16,17} The molecular weight remains predictable, and the polydispersity is low.

Finally, norbornenyl poly(δ VL) is another type of macromonomer that can be prepared by this cationic polymerization method. The ^1H NMR spectrum of poly(δ VL) initiated by 5-norbornene-2-methanol (NBOH)/ $\text{HCl}\cdot\text{Et}_2\text{O}$ and its M_n and M_w/M_n (entry 2f, Table 2) values confirm this. The terminal norbornenyl group can be (co)polymerized by ring-opening metathesis (ROMP), with formation of, e.g., poly(norbornene)-*graft*-

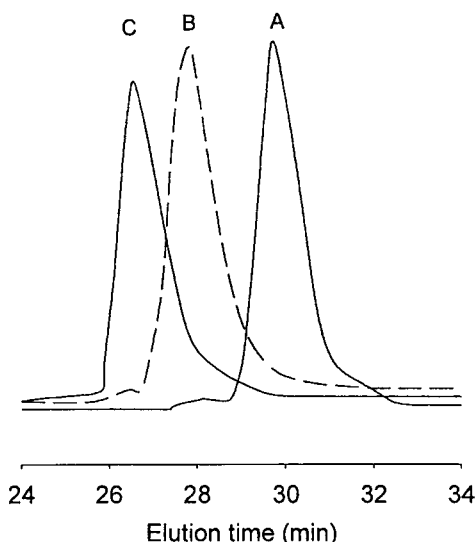


Figure 5. SEC chromatograms of (A) MPEG macroinitiator ($M_n = 2000$, $M_w/M_n = 1.08$), (B) MPEG-*b*-poly(δ VL) copolymer (3a; in Table 3, $M_n = 9500$, $M_w/M_n = 1.09$), (C) MPEG-*b*-poly(δ VL) copolymer (3b; in Table 3, $M_n = 16\,800$, $M_w/M_n = 1.09$).

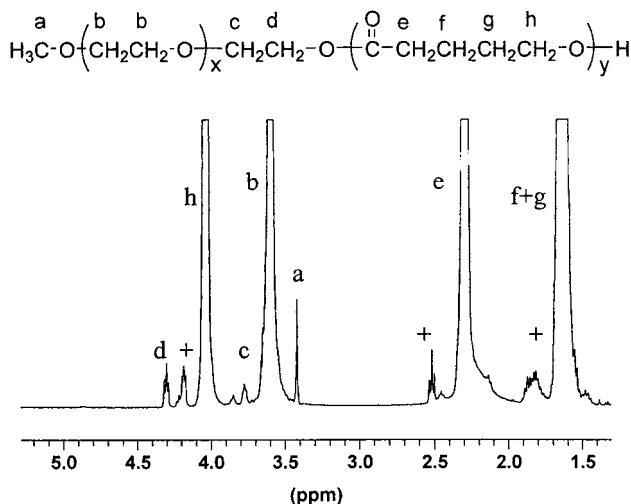


Figure 6. ^1H NMR spectrum of the MPEG-*b*-poly(δ VL) copolymer (3b; in Table 3). Signals marked by “+” refer to cyclics.

poly(δ VL) copolymers or high molecular weight comb-shaped poly(δ VL).¹²

The activated monomer polymerization of δ -VL is typically a direct way to control the synthesis of asymmetric telechelic polyesters. Compared to the coordinative ring-opening polymerization by functional aluminum alkoxide, the cationic polymerization is more direct because the alcohol is the actual initiator and not its precursor. Moreover, no metallic derivation is required, which leaves the final polymer free of undesirable contaminants.

Synthesis of Poly(ethylene oxide)-*b*-poly(δ VL) Di- and Triblock Copolymers. α -Methoxy- ω -hydroxyl-PEO (MPEG) and α,ω -dihydroxy-PEO (PEG) are potential macroinitiators for the cationic ROP of δ -VL in dichloromethane at 0 °C. The addition of $\text{HCl}\cdot\text{Et}_2\text{O}$ leads indeed to di- and triblock copolymers as confirmed by SEC and ^1H NMR analyses. Table 3 shows that the polymerization is almost quantitative within 3 h. The theoretical molecular weight of the poly(δ VL) block calculated from the monomer-to-hydroxyl group molar ratio and monomer conversion agrees well with the

experimental value extracted from the composition measured by ^1H NMR and M_n of PEG ($M_{n,\text{NMR}}(\text{PVL})$). Furthermore, the molecular weight distribution of the copolymer remains narrow ($M_w/M_n \sim 1.10$). Figure 5 compares the SEC chromatograms for the first MPEG block ($M_n = 2000$, $M_w/M_n = 1.08$) and the MPEG-*b*-Poly(δ VL) diblock copolymers (entries 3a and 3b; Table 3). The elution peak of the macroinitiator is systematically shifted toward higher molecular weight. It is not clear whether the faint tail observed on the low molecular weight side is due to contamination of MPEG by α,ω -methoxy-PEO or to slow initiation. Figure 6 shows the ^1H NMR spectrum and the peak assignment for the diblock copolymer 3b in Table 3 ($M_n = 16\,800$, $M_w/M_n = 1.09$). Peaks at 4.2 and 3.4 ppm can be assigned to the protons of the methoxy end group and the ethylene glycol unit adjacent to the poly(δ VL) block. This observation confirms the block copolymer formation. Because the block copolymerization is controlled, the composition of the amphiphilic copolymers can be extensively modified, as can their properties.

Conclusion

High molecular weight poly(δ VL) can be successfully prepared (at least up to $M_n = 50\,000$) by the activated monomer cationic ROP of δ -VL initiated by an alcohol/ $\text{HCl}\cdot\text{Et}_2\text{O}$ pair in dichloromethane at 0 °C. The molecular weight distribution is narrow (<1.10). Synthesis of poly(ϵ CL) of molecular weight higher than 15 000 remains a problem, however. Asymmetric telechelic poly(δ VL) can be directly synthesized by using an alcohol with the appropriate functionality. This alcohol forms the α end group, whereas a hydroxyl group is systematically the ω end group as result of hydrolysis of the propagating species. ROP of δ -VL initiated by macroinitiators, e.g., hydroxyl end-capped polyether, can lead to well-controlled di- or triblock copolymers. The alcohol/ $\text{HCl}\cdot\text{Et}_2\text{O}$ cationic initiator has the advantage of producing (co)polymers free from any metallic residue.

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