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Chemoenzymatic Synthesis of New Brush Copolymers Comprising Poly(ω-pentadecalactone) with Unusual Thermal and Crystalline Properties

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ABSTRACT: Lipases from different sources were screened to determine their relative performance to catalyze ω-pentadecalactone (PDL) ring-opening polymerization from the hydroxyl group of 2-hydroxyethyl methacrylate (2-HEMA) and ω-hydroxyl-ω'-methacrylate−poly(ethylene glycol) [PEGMA (M_n 360)]. Novozym 435 was found to be the most active biocatalyst for 2-HEMA/PEGMA-initiated PDL ring-opening polymerizations at 70 °C for 48 h in toluene (1:2 w/v of monomers). Thus, 2-HEMA-terminated PPDL was synthesized in yields of ∼80% and with <2 mol % carboxyl-terminated PPDL from initiation by water. Similarly, PEGMA-terminated PPDL was prepared. The free radical polymerizations of the corresponding macromers were carried out with AIBN at 70 °C in toluene. Thermal analysis of 2-HEMA-*co*-*b*-PPDL and PEGMA-*co*-*b*-PPDL macromers showed them to be stable and highly crystalline (T_m from 80 to 90 °C). In PEGMA-*co*-*b*-PPDL macromers, X-ray diffraction measurements show that the ethylene oxide units of the PEG block crystallize in the PPDL lattice. The main change observed upon polymerization of the macromers is a decrease of crystallinity (by both DSC and X-ray measurements).

Introduction

Brush polymers are formed when polymers are end-anchored in a sufficient concentration to a substrate. Polymer brushes with moderately high grafting densities have been prepared in the literature by harnessing the "grafting from" principle in which the polymer chains are synthesized using radical initiators that are covalently bound to the substrate. This has involved classical radical growth methods with either azo-(AIBN)- or peroxide-based initiators that were attached directly to the substrate or were attached to the substrate via self-assembly.[1−4] More recently, formation of polymer brushes using surface-initiated "living" radical polymerization such as atom transfer radical polymerization (ATRP) has also been reported.[5,6] Acrylate/methacrylate-based poly(lactic acid) macromonomers have been synthesized by Shinoda and Matyjaszewski using tin octonate as the catalyst.[7] The macromonomer was then copolymerized using ATRP to obtain poly(methyl methacrylate)-*g*-poly(lactic acid) graft copolymers.[7]

Two principal synthetic methods have been used to prepare macromonomers based on oligomers of lactones, viz. (a) end-capping of oligo(lactone)s with suitable methacrylic derivatives[8−11] and (b) initiation of the lactone ring-opening by a methacrylic derivative with a suitable initiating group.[12−14] Hedrick and co-workers[15,16a] have demonstrated the sequential and concurrent polymerizations of ϵ-caprolactone-2-bromo-2-dimethylpropionate with 2-hydroxyethyl methacrylate. This polymerization method allows simple control of the branch density and distribution by the selection of the polymerization method and monomer feed ratio. The introduction of controlled branching leads to polymers with well-defined and "tunable" macromolecular architectures.

The past 15 years have brought remarkable progress to enzyme-catalyzed transformations of a variety of small molecules.[17] The rational for using enzymes as catalysts has been described at length elsewhere.[17] Lipases are now well-established as alternative catalysts for lactone ring-opening polymerizations.[18,19] For four- to seven-membered ring lactones, traditional chemical catalysts provide high polymerization efficiencies.[18i] However, these catalysts generally lack the selectivity of lipases. Furthermore, because of the very different structure of organometallic and lipase catalysts, these systems often have different comonomer reactivity coefficients.[19c,d] Unlike small (four- to seven-membered) cyclic lactones that have ring strain, macrolactone polymerizations by chemical catalysis generally are slow and give low molecular weight polymers.[20] Fortunately, lipases are excellent catalysts of macrolactone ring-opening polymerizations that appear to be more efficient than alternative chemical systems.[19]

High molecular weight poly(ω-pentadecalactone), PPDL, has recently become available for physical studies due to its facile synthesis by lipase-catalyzed ring-opening polymerization of ω-pentadecalactone (PDL).[18b] PPDL is a crystalline polymer that melts close to 100 °C, has a glass transition below room temperature (−27 °C), and shows good thermal stability.[21] The crystal structure of the polyester[22] is similar to that of poly(ϵ-caprolactone). PPDL is a hard tough material with mechanical properties resembling those of low-density polyethylene. Recent work[23] on copolyesters containing ω-pentadecalactone units has revealed a marked tendency of the comonomers to cocrystallize. PDL copolymers show high levels of crystallinity and interesting

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physical properties. Unlike low-density polyethylene, PPDL has hydrolyzable ester links. These ester units regularly placed along the chain may lead to future use of PPDL as a biodegradable plastic and bioresorbable medical material.

This paper reports the synthesis and characterization of new vinyl polymers that have PPDL brushes of variable density and chain length. These polymers were prepared from either 2-hydroxyethyl methacrylate (2-HEMA) or ω-hydroxyl-ω'-methacrylate−poly(ethylene glycol) (PEGMA) and ω-pentadecalactone (PDL) by (i) first initiating PDL ring-opening oligomerization from either 2-HEMA or PEGMA using lipase catalysis and (ii) taking the product from (i) and catalyzing its free-radical polymerization by AIBN initiation. PDL was chosen as the lactone since it confers interesting crystalline and physical properties to its corresponding polymers (see above) and is efficiently polymerized by lipase catalysis and not by chemical systems (see above). Free-radical polymerization of 2-HEMA-*co*-*b*-PPDL and PEGMA-*co*-*b*-PPDL with different PPDL block lengths lead to a new family of dense brush homopolymers. The thermal and crystalline properties of the macromers and their corresponding copolymers were studied by thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and wide-angle X-ray diffraction (WAXS). The effect of the mobility restrictions caused by polymerization on PPDL crystallization was studied. Furthermore, the remarkable ability of the PPDL block to induce crystallization of PEG segments in an extended zigzag conformation was discovered.

Experimental Section

Materials. ω-Pentadecalactone (PDL), 2-hydroxyethyl methacrylate (2-HEMA), ω-hydroxyl-ω'-methacrylate−poly(ethylene glycol) (PEGMA, $M_n \sim 360$), poly(ethylene glycol) (PEG) with $M_n = 2000$, AIBN, and toluene were all purchased from Aldrich Chemical Co. Inc. in the highest available purity. Toluene was dried over calcium hydride and distilled under a nitrogen atmosphere. Poly(ω-pentadecalactone), PPDL, with number-average molecular weight (M_n) and polydispersity (PD) of 65 000 g mol^{-1} and 2.0, respectively, was synthesized as described elsewhere.[24] Coulomat A and Coulomat C were purchased from EM Science. Porcine pancreatic lipase (PPL) type II crude (activity = 61 units/mg of protein) and *Candida cylinderacea* lipase (CCL) type VII (activity = 4570 units/mg of protein) were obtained from Sigma Chemical Co. The lipases PS-30, PSC, AK, and AY from *Pseudomonas cepacia*, *Pseudomonas cepacia* on Celite, *Pseudomonas fluoroscens*, and *Candida rugosa*, respectively, were obtained from Amano Enzymes Co., Ltd., Lombard, IL. The activities as given by the manufacturer at pH 7.0 are 30 000, 30 000, 20 000, and 30 900 units/g, respectively. Immobilized lipases from *Candida antartica* (Novozyme 435) (7000 units/g) and *Mucor miehei* (Lipozyme IM) were gifts from Novozymes (Denmark). All enzymes prior to their use were dried over P_2O_5 (0.1 mmHg, 25 °C, 24 h). The amount of catalyst used was normalized with respect to their protein content.

Instrumental Methods. Proton (^{1}H) and carbon (^{13}C) NMR spectra were recorded on a Bruker Instruments Inc. DPX300 spectrometer at 300 and 75.13 MHz, respectively. The chemical shifts in parts per million (ppm) for ^{1}H and ^{13}C NMR spectra were referenced relative to tetramethylsilane (TMS) as an internal reference at 0.00.

Scheme 1. Chemoenzymatic Route to Brush Copolymers

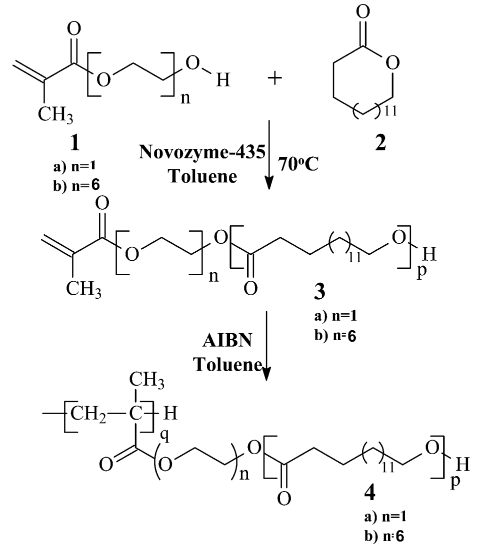

Table 1. Comparative Efficiency of 2-HEMA-Initiated PDL Polymerization Using Different Lipases[a]

entry	enzyme	% yield[c]	DP[d]	mol % carboxyl terminal chains[d]	PDI[e]
1	Novozym 435	88	14	<2	1.6
2	Lipase PSC	81	10	9	1.6
3	PPL	81	6	9	2.1
4	Lipase AY	75	5	9	1.3
5	PS-30	52	6	10	1.3
6	CCL	35	6	15	1.1
7	Lipase AK	30	3.2	11	1.2
8	Lipozym	13	1.2	7	1.5
9	Novozym 435[b]	87	6.0	<2	1.4

[a] The molar ratio of 2-HEMA to PDL was 1:10 unless noted otherwise. [b] The molar ratio of 2-HEMA to PDL was 1:5. [c] The % yield was calculated as the weight ratio of the dried methanol precipitated product to the monomer charged multiplied by 100. [d] Determined by ^{1}H NMR analysis of the precipitated product. [e] Determined by GPC measurements.

NMR spectra of 2-HEMA-*co*-b-PPDL (Scheme 1, **3a**) ($CDCl_3$) $CH_2{}^h{=}C(CH_3{}^g)-(C{=}O)-O-CH_2{}^f-CH_2{}^e-O-[-(C{=}O)-CH_2{}^b-CH_2{}^c-\{-CH_2{}^d-CH_2{}^d-\}_5-CH_2{}^c-CH_2{}^a-O-]_m-H$ (entry 1, Table 1) was as follows: ^{1}H NMR ($CDCl_3$) δ 6.09 and 5.55 [brs, $CH_2{}^h{=}C(CH_3)$], 4.25 (brs, $CH_2{}^e$), 4.11 (t, 6.6 Hz, $CH_2{}^f$), 4.07 (t, J 6.5 Hz, $CH_2{}^aO$), 3.61 (t, J 6.5 Hz, CH_2OH), 2.31 (t, J 7.5 Hz, $CH_2{}^bCO$), 1.92 [s, $C(CH_3{}^g)$], 1.65 and 1.30 ppm (brs, $CH_2{}^{c,d}$). ^{13}C NMR ($CDCl_3$) δ 173.7 ($COCH_2$), 173.3 ($CH_2{}^eOCO$), 167.2 [$COC(CH_3)$], 136.5 [$C(CH_3)$], 124.4 [$CH_2{=}C(CH_3)$], 64.52 ($CH_2{}^fO$), 64.4 ($CH_2{}^aO$, $CH_2{}^eO$), 61.8 (CH_2OH), 34.4 ($OCOCH_2{}^b$), 34.0 ($COCH_2{}^b$ end group), 18.1 [$C(CH_3)$], 29.6−29.1, 28.6, 25.9, and 25.0 ppm (all other carbons).

NMR spectra of poly(2-HEMA-*co*-b-PPDL) (**4a**) ($CDCl_3$) $-[-CH_2{}^h-C(R)(CH_3{}^g)-]_n-$ where R is $(C{=}O)-O-CH_2{}^f-CH_2{}^e-O-[(C{=}O)-CH_2{}^b-CH_2{}^c-\{-CH_2{}^d-CH_2{}^d-\}_5-CH_2{}^c-CH_2{}^a-O-]_m-H$ was as follows: ^{1}H NMR ($CDCl_3$) δ 4.25 (s, $OCH_2{}^e$), 4.0 (t, J 6.5 Hz, $OCH_2{}^{a,f}$), 3.68 (t, J 6.5 Hz, CH_2OH), 2.31 (t, J 7.5 Hz, $CH_2{}^bCO$), 1.65 and 1.30 ppm (brs, $CH_2{}^{c,d}$ and $CH_3{}^g$). ^{13}C NMR ($CDCl_3$) δ 173.9, 173.54, 72.5, 70.6 and 70.7, 69.1, 64.8, 64.3, 64.4, 63.3,62.9, 34.4, 34.14, 32.76, 29.6−29.1, 28.6, 25.9, and 25.0 ppm.

NMR spectra of PEGMA-*co*-b-PPDL (**3b**) ($CDCl_3$) $CH_2{}^h{=}C(CH_3{}^g)-(C{=}O)-O-[CH_2{}^f-CH_2{}^e-O-]_m-[(C{=}O)-CH_2{}^b-CH_2{}^c-\{-CH_2{}^d-CH_2{}^d-\}_5-CH_2{}^c-CH_2{}^a-O-]_0-H$ (entry 10, Table 2) was as follows: ^{1}H NMR ($CDCl_3$) δ 6.09 [brs,$CH_2{}^h{=}C(CH_3)$], 5.55 [brs, J 1.76 Hz, $CH_2{}^h{=}C(CH_3)$], 4.25 (brs, J 4.75 Hz, $OCO-CH_2{}^e$), 4.13 (brs, J 6.76 Hz, $OCOCH_2{}^f$), 4.07 (t, J 6.5 Hz, $CH_2{}^aO$), 3.58−3.68 (brm, CH_2OH and CH_2CH_2O (PEG)), 2.31 (t, J 7.5 Hz, $CH_2{}^bCO$), 1.65 and 1.30 (brs, $CH_2{}^{c,d}$), 1.92 ppm [m, $C(CH_3{}^g)$]. ^{13}C NMR ($CDCl_3$) δ 173.9 ($\mathbf{C}OCH_2$), 173.7 [$COC(CH_3)$], 136.25 and 124.92 ($C{=}CH$), 72.5(OCH_2), 70.6 and 70.7 (OCH_2), 69.1 (OCH_2), 64.8, 64.3, 64.4 ($\mathbf{C}H_2{}^aO$), 63.3, 62.9 (CH_2OH), 34.4 ($OCO\mathbf{C}H_2{}^b$), 34.14 (CH_2), 32.76 [$C(CH_3)$], 29.6−29.1, 28.6, 25.9, and 25.0 ppm (all other carbons).

NMR spectra of poly(PEGMA-*co*-b-PPDL) (**4b**) ($CDCl_3$) $-[CH_2{}^h-C(R)(CH_3{}^g)]_n-$ where R is $(C{=}O)-O-[CH_2{}^f-CH_2{}^e-$

Table 2. Comparative Efficiency of PEGMA-Initiated PDL Polymerization Using Different Lipases[a]

entry	enzyme	% yield[c]	DP[d]	mol % carboxyl terminal chains[d]	PDI[e]
10	Novozym 435	82	5	<2	1.5
11	Lipase AY	2	N.D	7	1.6
12	Lipase AK	28	6	14	1.3
13	Liposyme	2	5	13	N.D
14	Lipase PSC	66	6	11	1.2
15	CCL	44	5	14	1.9
16	PPL	80	6	10	1.7
17	Lipase PS 30	66	20	5	1.4
18	Novozym 435[b]	88	11	<2	1.6

[a] The molar ratio of PEGMA to PDL was 1:5 unless noted otherwise. [b] The molar ratio of PEGMA to PDL was 1:10. [c] The % yield was calculated as the weight ratio of the dried methanol precipitated product to the monomer charged multiplied by 100. [d] Determined by ^{1}H NMR analysis of the precipitated product. [e] Determined by GPC measurements.

$O{-}]_m{-}[(C{=}O){-}CH_2{}^b{-}CH_2{}^c{-}\{{-}CH_2{}^d{-}CH_2{}^d{-}\}_5{-}CH_2{}^c{-}CH_2{}^a{-}O{-}]_0{-}H$ was as follows: ^{1}H NMR ($CDCl_3$): 4.25 (brs, J 4.75 Hz $O{-}C({=}O){-}CH_2{}^e$), 4.13 (brs, J 6.76 Hz, $CH_2{}^f$), 4.07 (t, J 6.5 Hz, $CH_2{}^aO$), 3.61 (t, J 6.5 Hz, CH_2OH), 2.31 (t, J 7.5 Hz, $CH_2{}^b$-CO), 1.65 and 1.30 (brs, $CH_2{}^{c,d}$), 1.92 ppm [m, $C(CH_3{}^g)$]. ^{13}C NMR ($CDCl_3$) δ 173.9 ($\mathbf{C}OCH_2$), 173.7 [$COC(CH_3)$], 72.5 (OCH_2), 70.6 and 70.7 (OCH_2), 69.1 (OCH_2), 64.8, 64.3, 64.4 ($\mathbf{C}H_2{}^aO$), 63.3, 62.9, 34.4 ($OCO\mathbf{C}H_2{}^b$), 34.14 (CH_2), 32.76-[$C(CH_3)$], 29.6−29.1, 28.6, 25.9, 25.85, 25.0, and 24.9 ppm (all other carbons).

Reaction initial water contents (wt % water) were measured by using an Aqua star C 3000 titrator with Coulomat A and Coulomat C from EM Science. The water w/w in reaction mixtures was determined by stirring 53 mg of catalyst, 1.68 g of dried toluene, and 0.53 g of monomer in coulomat A in a closed septum container designed in the instrument and titrating it against coulomat C by the instrument. The total water content (w/w) in the reactions was ~1.0−1.5%. Since >95% of the reaction water content is from that remaining in the enzyme−catalyst system, the enzyme−water content is nearly identical to the total reaction water content.

Powder wide-angle X-ray patterns were recorded from $2\theta = 2.5°$ to $2\theta = 60°$ with a Philips PW 1050/81 diffractometer, equipped with a graphite monochromator in the diffracted beam and using Cu Kα radiation at $\lambda = 0.1542$ nm (40 kV, 40 mA). Thermogravimetric (TGA) measurements were carried out using a TA-TGA 2950 under N_2 flow. Sample weight was in the range 7−10 mg. The analyses were performed at 10 °C/min from room temperature to 600 °C. Differential scanning calorimetry (DSC) was performed using a TA-DSC 2010. The temperature scale was calibrated with high-purity standards. After a first heating run at 20 °C/min to 120 °C to cancel the effects of previous thermal history, the sample was cooled at 10 °C/min to −80 °C and subsequently heated at 20 °C/min from −80 to 120 °C. The crystallization and melting temperatures (T_c and T_m) are taken from the DSC curves of the cooling and heating scans, respectively, as the peak temperature of the thermal event.

General Procedure: Synthesis of 2-HEMA-*co*-b-PPDL and PEGMA-*co*-b-PPDL. Novozyme 435 (0.075 g), dried in a vacuum desiccator (0.1 mmHg, 25 °C, 24 h), was transferred under a nitrogen atmosphere into oven-dried 10 mL Pyrex culture tubes containing PDL (5 mmol). The vials were stoppered with rubber septa and sealed with Teflon tape. PEGMA or 2-HEMA (1 mmol) was added via syringe under nitrogen into the reaction vials. Toluene (twice w/v of monomers) was subsequently added via syringe under nitrogen into the reaction vials. The vials were then placed into a constant temperature (70 °C) oil bath with magnetic stirring (220 rpm) for 48 h. At 70 °C, mixtures of PDL and PPDL form a monophasic liquid.[19c] Reactions were terminated by adding excess cold chloroform and removing the enzymes by filtration (glass-fritted filter, medium pore porosity). The insoluble portion was washed several times with hot chloroform. The chloroform in the filtrate was in large part removed by rotary evaporation, and the polymer in the concentrated solution was precipitated in methanol. The precipitate was isolated by filtration and then dried in a vacuum oven (0.1 mmHg, 50 °C, 24 h). The % yield given in Tables 1 and 2 was calculated as the weight ratio of the dried precipitated product to the monomer charged multiplied by 100. The DP of the PPDL block was determined by ^{1}H NMR while the PDI was measured by GPC (see above).

General Procedure: AIBN Polymerization of 2-HEMA-*co*-b-PPDL and PEGMA-*co*-b-PPDL. AIBN dried in a vacuum desiccator was transferred into oven-dried 10 mL Pyrex culture tubes containing the macromer (**3a** or **3b**). The vials were stoppered with rubber septa and sealed with Teflon tape. Dry distilled toluene was added to the above mixture, and the reactions were kept for predetermined time periods in an oil bath maintained at 70 °C. The resulting product was precipitated in methanol. The precipitated material was dried in a vacuum oven (0.1 mmHg, 50 °C, 24 h).

Results and Discussion

Macromers are functional oligomers or low molecular weight polymers that are polymerizable. Previous work has shown that primary hydroxyl groups in small molecules such as butanol,[18f] ethylglucoside,[18d] 4-hydroxyphenylethanol, and others[24b] can be initiators or acyl acceptors for the lipase-catalyzed ring-opening polymerizations of ϵ-caprolactone. The mechanism by which these reactions occur is likely by reaction of serine, present in the catalytic active site of the lipases, with lactones to form acyl-enzyme-activated monomer (EAM).[18f,24b,c] This EAM can react with small molar mass initiators to form ester-terminated $R{-}O{-}[C{=}O]{-}CH_2{-}$ (R is initiator) chains. Further reactions between the propagating chain end and the EAM can further increase the chain length. Also, lipases actively catalyze the cleavage of intrachain ester groups of nonbranched aliphatic polyesters to give enzyme-activated chain segments (EACS).[24d] The terminal hydroxyl group of another macromolecule can subsequently react with the EACS to give an ester group. Another possibility is initiation of chains by water to give HOOC-terminated poly(lactones). These carboxyl-terminated chains can persist in the reaction or may condense with a hydroxyl group at a chain end or of the initiator.[24e]

Illustrative examples of how macromer structure was analyzed by ^{1}H NMR are as follows. Spectra of products from Novozym 435-catalyzed ring-opening polymerization of PDL at 70 °C in toluene using 2-HEMA (**1a**) and PEGMA ($M_n \sim 360$) (**1b**) as initiators are shown in Figures 1 and S1 (Supporting Information), respectively. The monomer:solvent ratio was 1:2 w/v, and the ratio of 2-HEMA or PEGMA to PDL was 1:10 mol/mol. The ^{1}H NMR signal at 3.65 (t) for the products was assigned to the methylene ($-CH_2OH$) groups at the hydroxyl chain terminus. The signals between 3.5 and 3.7 ppm are characteristic of the main-chain methylene units of PEG.[24e] During lipase-catalyzed lactone polymerization, the ^{1}H NMR signals due to the methylene protons of terminal PEG units (CH_2OH) shift from 3.5 to 3.7 ppm to 4.24 ppm. This is due to the formation of an ester link with the carboxyl terminal end of a propagating polyester chain. Derivatization of the copolymer products with oxalyl chloride was used to further resolve ^{1}H NMR signals of end groups.[24e] This derivatization caused downfield shifts of the terminal PEG and poly(PDL) CH_2OH protons to 4.48 ppm (t) and 4.34 ppm (t), respectively. If, instead of 2-HEMA or PEGMA, water acts as a nucleophile for chain initiation and/or transacylation reactions, then poly(PDL) chains will be formed with terminal carboxyl groups. Derivatization with oxalyl chloride of terminal carboxyl groups in products would give a ^{1}H NMR signal at ~2.9 ppm. However, using PEGMA as the initiator or acceptor for acyl transfer reactions, a signal at ~2.9 ppm was not found. Hence, we conclude that initiation with water was not observed. This was further supported by the absence of a ^{13}C NMR signal at 177.5 ppm that would have been generated if chain end carboxylic acids were formed. The degree of polymerization was calculated by taking the integral ratios of signals due to intrachain repeat unit $(O{=}C){-}OCH_2$ protons and the chain end α-methyl protons of the methacrylate moiety at 4.04 and 1.9 ppm, respectively. Similar studies as above were performed by using 2-HEMA in place of PEGMA as the initiator for lipase-catalyzed PDL polymerizations. The results of this work are further elaborated below.

Lipase Screening. A number of lipases were evaluated for their activity to use 2-HEMA (**1a**) and PEGMA ($M_n \sim 360$) (**1b**) as initiators for PDL polymerizations. The reactions were conducted at 70 °C, in toluene (monomer:solvent 1:2 w/v), for 48 h, with the ratio of initiator (2-HEMA or PEGMA) to PDL of 1:10 mol/mol. The lipases studied include PS-30, AK, AY, PSC, PPL, CCL, immobilized CALB (Novozym 435), and Lipozyme IM from *Mucor meihei* (see Experimental Section). All of these enzyme−catalyst systems were dried over P_2O_5 (0.1 mmHg, 25 °C, 24 h) prior to use. This resulted in nearly identical total water (1.0−1.5% w/w) in the reactions with different lipases.

The choice of lipase was based on rapid monomer conversion with high 2-HEMA and PEGMA initiation efficiency. The result would be macromers with a polymerizable vinyl group at the carboxyl chain terminus. Presumably, water-initiated macromers would not participate in the subsequent free-radical polymerization. Listed in Tables 1 and 2 are the results with different lipases of PDL polymerization using 2-HEMA and PEGMA, respectively, as chain initiatiors. The % yields in Tables 1 and 2 were determined from the weight of the solvent precipitated product. ^{1}H NMR analysis of products was used to determine the absolute average degree of polymerization (DP) of PDL units attached to 2-HEMA and PEGMA. In contrast, since GPC analyses used polystyrene standards, they give relative values that can be misleading. Thus, the discussion of DP is based on results obtained from ^{1}H NMR. GPC was used to obtain an estimate of macromer polydispersity (M_w/M_n, PDI). Furthermore, as described above, ^{1}H NMR end group analysis of oxalyl chloride modified macromers was used to measure the mol % of carboxyl-terminated chains.

Inspection of Table 1 shows Novozym 435 is best for 2-HEMA-initiated PDL polymerization. With Novozym 435, the product was obtained in 88% yield (entry 1, Table 1). Derivatization with oxalyl chloride revealed that <2 mol % of the chains formed had carboxyl terminal groups. Lipases PSC, PPL, and AY also gave high product yields (75−81%). The products had DP of 10, 6, and 5, respectively. Also, lipases PSC, PPL, and AY formed products where 9 mol % of the chains had carboxyl terminal groups (entries 2−4, Table 1). Lipases CCL, AK, and Lipozyme gave low DP products in poor yields (≤35%) (entries 6−8, Table 1). Predictably, by changing the 2-HEMA to PDL ratio from 1:10 to 1:5 and by using Novozyme 435, the macromer DP decreased from 14 to 6 (entries 1 and 9, Table 1). Furthermore, the mol % of carboxyl terminal chains remained low (<2 mol %), and the product yield was 87% (entry 9, Table 1). Similar results were also observed when PEGMA was used instead of 2-HEMA as the initiator for PDL polymerization (Table 2). Comparison of Tables 1 and 2 shows that lipase AY was remarkably more efficient when 2-HEMA was the initiator. Also, Lipase PS 30 gave PEGMA-*co*-b-PPDL and 2-HEMA-*co*-b-PPDL with PDL block lengths of 20 and 6, respectively. This occurred despite that the molar ratios of PEGMA to PDL and 2-HEMA to PDL were 1:5 and 1:10, respectively. This suggests that PS 30 catalyzed PDL oligomerization initiated by PEGMA occurred with low initiator efficiency. Furthermore, even though PEGMA initiator efficiency is low, PEGMA initiation still dominated over initiation by water so that the chains formed had only 5 mol % carboxyl terminal groups. These changes in initiator efficiency as a function of the initiator structure, relative concentration of water, monomer structure, and the lipase origin are not currently understood on a molecular basis.

Table 3. Novozyme 435-Catalyzed 2-HEMA/PEGMA-Initiated PDL Polymerization

entry	initiator	molar feed (PDL:2-HEMA/PEGMA)	DP[a]
19	2-HEMA	2:1	2
20	2-HEMA	4.5:1	5
21	2-HEMA	9.5:1	11
22	PEGMA	1:1	1.5
23	PEGMA	2:1	2
24	PEGMA	5:1	5.5

[a] Determined by ^{1}H NMR analysis of the precipitated product.

Studies performed where the ratio of PDL to 2-HEMA and PEGMA was varied suggest that initiation and transesterification reactions are sufficiently rapid to effect the resulting macromer DP. Thus, when the ratio of 2-HEMA to PDL was changed from 1:5 to 1:10, the macromer DP's were 6 and 14, respectively. Similarly, for PEGMA to PDL ratios of 1:5 and 1:10, the DP's of the PPDL chain segments were 5 and 11, respectively. This knowledge was then applied to prepare macromers of controlled chain length and, subsequently, polymers with controlled branch dimensions. When the ratios of 2-HEMA to PDL were 1:2, 1:4.5, and 1:9.5, 2-HEMA-*co*-b-PPDL with average PPDL DPs of 2, 5, and 11 were obtained (entries 19−21, Table 3). Similarly, when the ratios of PEGMA to PDL were 1:1, 1:2, and 1:5, PEGMA-*co*-b-PPDL with average PPDL DPs of 1.5, 2, and 5.5 were prepared (entries 22−24, Table 3). The isolation step, when the macromers were precipitated into methanol, removed unreacted 2-HEMA and PEGMA. These macromers were then polymerized by a free radical mechanism using AIBN as the initiator at 70 °C in toluene.

The brush polymers from 2-HEMA-*co*-b-PPDL (PPDL DP 2, 5, and 11) and PEGMA-*co*-b-PPDL (PPDL DP 1.5, 2, and 5.5) were obtained in yields of 80−85%. Without exception, the polymers showed poor solubility in chloroform, dichloromethane, carbon tetrachloride, dimethylformamide, dimethyl sulfoxide, methanol, and dioxane. A general decrease in the solubility of the comb polymers was observed as the length of PPDL branches was increased. This is consistent with observations made by Hedrick et al.[16a] and Hawker et al.[16b] They observed that copolymers with high contents of cyclic ester, γ-(2-bromo-2-methyl propionyl)-ϵ-caprolactone,

Table 4. Thermal Properties of 2-HEMA-*co*-b-PDL Macromers and Polymers

		TGA		DSC					
				as prepared		cooling		reheating	
sample	DP	Δm (RT − 300 °C) (wt %)	T_{max} (°C)	T_m (°C)	ΔH_m (J/g)	T_c (°C)	ΔH_c (J/g)	T_m (°C)	ΔH_m[a] (J/g)
2-HEMA-*co*-b-PPDL[b]	2	2.2	436	81	187	60	124	78	130
2-HEMA-*co*-b-PPDL[c]	5	1.6	432	87	185	72	154	87	157
2-HEMA-*co*-b-PPDL[d]	11	0.8	435	90	179	73	157	89	164
P(2-HEMA-*co*-b-PPDL)	2	1.4	437	81	117	57	97	79	105
P(2-HEMA-*co*-b-PPDL)	5	1.0	436	82	135	63	121	82	126
P(2-HEMA-*co*-b-PPDL)	11	0.8	436	89	148	68	128	89	137
PPDL		0.7	434	96	164	78	131	98	143

[a] Per gram of whole sample. [b] Entry 19 in Table 3. [c] Entry 20 in Table 3. [d] Entry 21 in Table 3.

Table 5. Thermal Properties of PEGMA-*co*-b-PPDL Macromers and Polymers

		TGA		DSC						
				as prepared		cooling		reheating		
sample	DP	Δm (RT − 300 °C) (wt %)	T_{max} (°C)	T_m (°C)	ΔH_m (J/g)	T_c (°C)	ΔH_c (J/g)	T_m (°C)	ΔH_m[a] (J/g)	$\Delta H_{m(PDL)}$[b] (J/g$_{PDL}$)
PEGMA-*co*-b-PPDL[c]	1.5	2.5	434	79	160	64	123	77	136	267
PEGMA-*co*-b-PPDL[d]	2	1.8	436	87	193	71	151	86	156	269
PEGMA-*co*-b-PPDL[e]	5.5	2.1	435	89	184	74	147	89	158	200
P(PEGMA-*co*-b-PPDL)	1.5	1.8	435	68	88	49	85	71	90	176
P(PEGMA-*co*-b-PPDL)	2	1.0	435	86	141	71	130	87	136	234
P(PEGMA-*co*-b-PPDL)	5.5	1.2	434	88	150	74	141	88	143	181
PPDL		0.7	434	96	164	78	131	98	143	143

[a] Per gram of whole sample. [b] Per gram of PDL. [c] Entry 22 in Table 3. [d] Entry 23 in Table 3. [e] Entry 24 in Table 3.

gelled upon polymerization because of coupling reactions of radicals with the formation of network. The scarce solubility of these PPDL comb polymers did not permit the analysis of their molecular weights.

The thermal properties of the macromers and of their corresponding polymers were investigated and are summarized in Tables 4 and 5. Thermal properties of PPDL reported in an earlier study[21] are included for comparison. All macromers and polymers are thermally stable up to high temperatures, as shown by the results of the TGA measurements (Tables 4 and 5). The TGA curves show a single weight loss step centered at a temperature (T_{max}) practically identical to that of PPDL. The only appreciable difference between the TGA curve of PPDL and those of the present samples is a slight gradual decrease of weight preceding the main degradation of the macromers and, to a lesser extent, of the corresponding polymers. The entity of this phenomenon is quite small so that the total weight loss observed at 300 °C for the different samples is between 1% and 2.5%. The extent of this weight loss decreases upon polymerization of the macromers and is probably associated with the methacrylate part of the molecule. The fact that the polymers are more thermally stable than the corresponding macromers is consistent with the expected molecular weight dependence of thermal stability[25] and also reflects the decrease upon polymerization of the number of unsaturated groups. These groups in polymethacrylates synthesized from radical polymerization have been shown[26] to be responsible for initiation of thermal degradation.

The main thermal events in the DSC curves of the macromers and polymers investigated are crystallization and melting, observed in the cooling and heating runs, respectively. The temperatures and enthalpies of the phase transitions of HEMA-*co*-b-PPDL and PEGMA-*co*-b-PPDL macromers and polymers are collected in Tables 4 and 5, respectively. Comparison of the melting temperature (T_m) of the various samples with that of PPDL suggests that it is the PDL part of the analyzed macromers and polymers that crystallizes and melts. With increasing length of the PDL block both the melting and crystallization temperatures increase in the macromers as well as in the polymers. This behavior reflects the formation of better crystals (larger and less defective) with increasing molecular weight of the PDL block.[27]

The melting enthalpy (ΔH_m) reflects the amount of crystallinity developed in each sample. It is appropriate to compare the thermal behavior of samples subjected to the same thermal history (reheating run in Tables 4 and 5). In all macromers investigated ΔH_m is quite high. In fact, in some cases, ΔH_m of the macromers is even higher than the experimental melting enthalpy of the high molecular weight PPDL homopolymer taken as a reference.

The macromers were crystallized upon cooling from the melt at 10 °C/min (same treatment as in DSC) and were subjected to X-ray diffraction analysis. All macromers investigated yielded the same X-ray pattern. As an example, Figure 2 shows the WAXS diffractograms of two macromers (2-HEMA-*co*-b-PPDL and PEGMA-*co*-b-PPDL, entries 19 and 23 in Table 3, respectively) with the same average PDL block length (DP = 2). The X-ray profile of both samples is the same as that of the homopolymer (also shown in Figure 2), confirming that the macromers crystallize in the PPDL crystal lattice.[22] The amorphous phase contribution to the X-ray diffractograms (see dashed curve in Figure 2) is smaller in the macromers than in PPDL; i.e., their degree of crystallinity is slightly higher than that of the homopolymer. Also, the average crystal size, estimated according to Scherrer's equation[28,29] from the half-width of the intense (110) reflection[22] at $2\theta = 21.5°$, is larger in the macromers than in PPDL (30 nm vs 22 nm, respectively). In conclusion, X-ray analysis shows that 2-HEMA-*co*-b-PPDL and PEGMA-*co*-b-PPDL macromers are able to develop a consistent fraction of crystallinity (55−57%

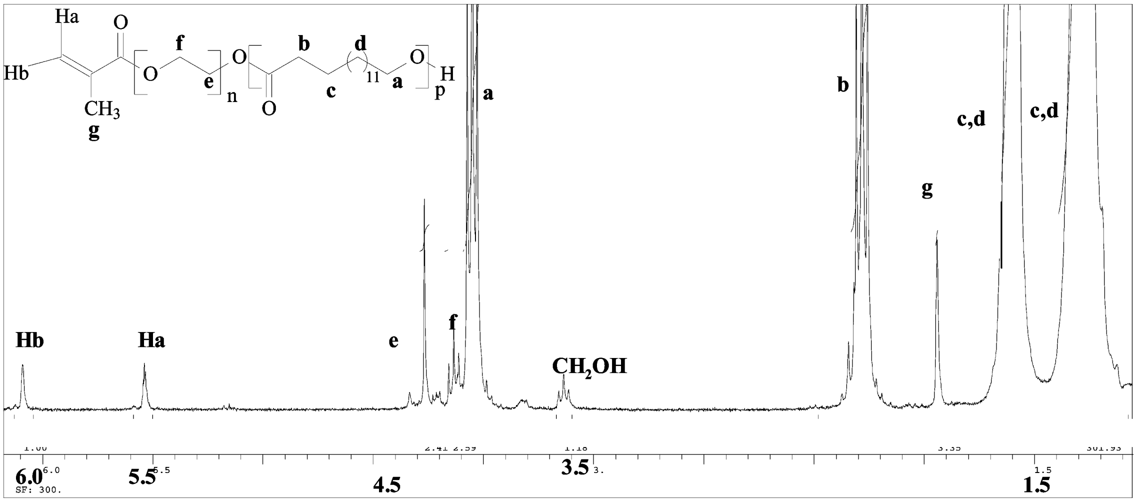

Figure 1. ^{1}H NMR spectrum of 2-HEMA-*co*-*b*-PPDL (entry 1, Table 1).

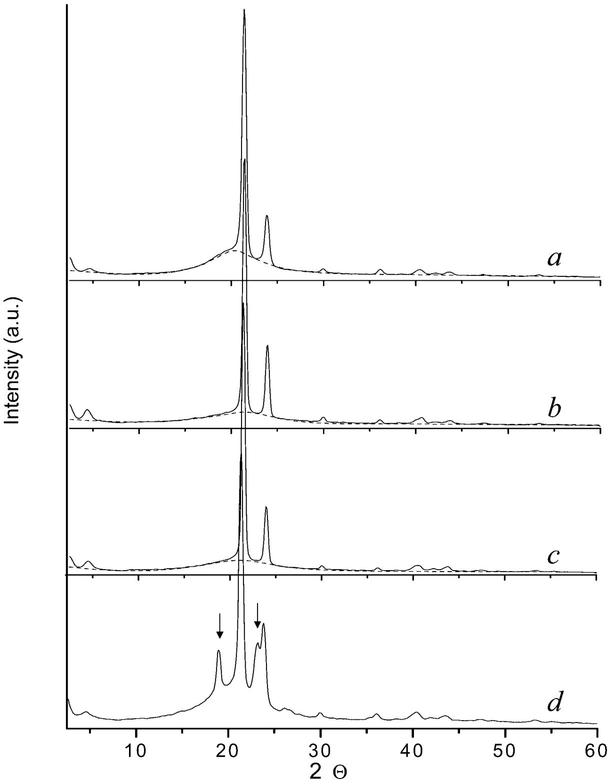

Figure 2. WAXS diffractograms of (a) PPDL, (b) 2-HEMA-*co*-b-PPDL (entry 19, Table 3), (c) PEGMA-*co*-b-PPDL (entry 23, Table 3), and (d) PPDL/PEG blend (65/35 by weight). Arrows mark the main PEG reflections.

in the samples of Figure 2) comprising crystals of large dimensions.

The melting enthalpy data listed in Tables 4 and 5 clearly show that, within the series of 2-HEMA-*co*-b-PPDL and PEGMA-*co*-b-PPDL macromers, ΔH_m increases with increasing PDL block length. This result is expected if it is the PDL block that crystallizes in the macromers. However, a point that cannot be straightforwardly explained is the high ΔH_m value of all PEGMA-*co*-b-PPDL macromers. It should be kept in mind that these macromers contain on average six ethylene oxide repeat units between the PDL block and the methacrylate end. Unless cocrystallization occurs, the PEG block should be excluded from the PPDL crystal phase and should not contribute to the observed melting enthalpy (ΔH_m in J/g). However, when the melting enthalpy is recalculated considering the PDL content of each sample ($\Delta H_{m(PDL)}$ in Table 5), unexpectedly high values are obtained (compared with ΔH_m of PPDL). This result suggests that in PEGMA-*co*-b-PPDL macromers the ethylene oxide units contribute to crystal phase formation.

At first sight this hypothesis may appear unrealistic on account of the different crystal cells of PPDL (pseudo-orthorhombic monoclinic, $a = 7.49$ Å, $b = 5.03$ Å, $c = 20.00$ Å, $\alpha = 90.06°$)[22] and of PEG (monoclinic, $a = 8.05$ Å, $b = 13.04$ Å, $c = 19.48$ Å, $\beta = 125.4°$)[30] and of the different crystal chain conformations of the two polymers: planar zigzag the former, 7_2 helix the latter. Figure 2 shows the X-ray diffractogram of a blend of PPDL with PEG ($M_n = 2000$) having the same ethylene oxide/PDL ratio as the PEGMA-*co*-b-PPDL macromer (entry 23, Table 3) and crystallized under the same experimental conditions. Unlike the PEGMA-*co*-b-PPDL macromer that only shows the typical reflections of PPDL crystals, the X-ray profile of the blend also shows the reflections of the PEG lattice (main reflections marked by arrows). This indicates that the two blended homopolymers develop their own crystal phase upon crystallization from the melt.

The high degree of crystallinity achieved by the PEGMA-*co*-b-PPDL macromers together with the total absence of PEG reflections in the X-ray profile of this compound (Figure 2) provide convincing evidence that, for these macromers, the ethylene oxide units of the PEG block crystallize in the PPDL lattice. Further support for this idea can be found in the literature, where poly(ethylene oxide) has been reported to crystallize in a zigzag conformation under particular conditions.[31,32] Both mechanical strain[31] and freeze-drying[32] have been shown to induce crystallization of poly(ethylene oxide) in a planar zigzag conformation. Moreover, in diblock PEG−PE oligomers used as surfactants, PEG sequences have been reported to crystallize in an extended all-trans conformation, depending on the length of the blocks and on the experimental crystallization conditions. [33,34]

Unlike the PEG/PPDL blend discussed above, where the homopolymer components independently crystallize upon cooling (PPDL at a higher temperature then PEG), in the present PEGMA-*co*-b-PPDL macromers the PEG sequence is covalently linked to the PPDL block. Crystallization of the PPDL block is likely to generate a

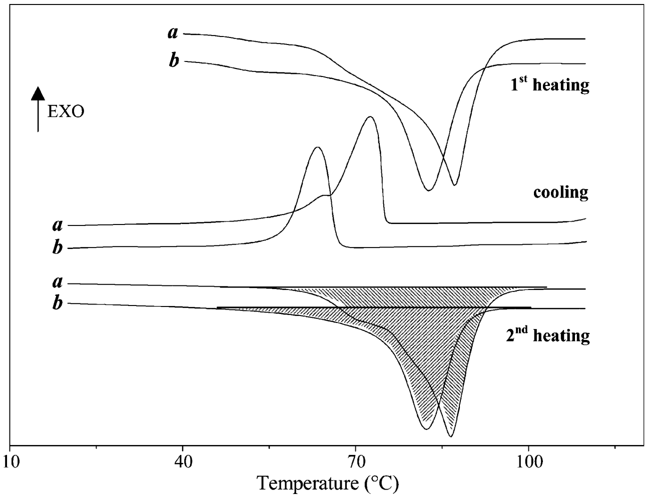

Figure 3. DSC curves (first heating, 20 °C/min; cooling, 10 °C/min; reheating, 20 °C/min) of (a) 2-HEMA-*co*-b-PPDL (entry 20, Table 3) and (b) P(2-HEMA-*co*-b-PPDL) with DP = 5.

stress on the covalently linked PEG chain. This stress then induces the linked PEG chain to assume an extended zigzag conformation and to crystallize in the PPDL crystal lattice. This phenomenon contributes to the high crystallinity of the present macromers.

The melting enthalpy results, listed in Tables 4 and 5, allow comparison of the thermal properties of 2-HEMA-*co*-b-PPDL and PEGMA-*co*-b-PPDL macromers with those of the corresponding polymers. Figure 3 shows as an example the DSC curves of 2-HEMA-*co*-b-PPDL macromer (entry 20, Table 3) and of the corresponding P(2-HEMA-*co*-b-PPDL). The main change observed upon polymerization of all macromers is a decrease of crystallinity (see ΔH_m), also confirmed by X-ray measurements. This result may be explained by the mobility restriction that occurs when the macromer units become covalently linked in the polymethacrylate chain. The crystallizable part of the polymers is constituted by the pendant side chains. Furthermore, the polymers obtained by radical polymerization are expected to be atactic. The enthalpy results of Tables 4 and 5 show that the likely lack of stereoregularity does not prevent crystallization of the long crystallizable side chains. However, stereo-irregularities probably hinder ordering and packing of side-chain segments close to the polymer backbone, thus lowering the overall degree of crystallinity. Earlier results[35] on atactic poly(*n*-alkyl acrylates) with long alkyl side chains showed that 10−12 methylene units close to the main chain stay in the amorphous state, whereas the remaining outer alkyl chain segment crystallizes. In the present polymers, especially in P(PEGMA-*co*-b-PPDL), the crystal phase fraction remains quite large, though smaller than in the original macromers (Tables 4 and 5). The X-ray diffractograms of P(PEGMA-*co*-b-PPDL) (not reported) only show the typical PPDL crystal lattice reflections, as was already described for PEGMA-*co*-b-PPDL macromers (Figure 2). This result, together with the high melting enthalpy of P(PEGMA-*co*-b-PPDL), is evidence that even in the polymers the PEG units cocrystallize with the PDL sequences.

Conclusions

A simple and mild route was developed to form well-defined macromers that are useful for the introduction of amphiphilic or hydrophobic side groups into polyvinyls. Novozyme 435 was found to be the most active biocatalyst for 2-HEMA- and PEGMA-initiated PDL polymerizations. Thus, this method gave macromers consisting of 2-HEMA or PEGMA linked to a PDL oligoester chain segment. The degree of polymerization of the polyester chain segment was easily "tuned" by the lactone/initiator ratio that was used. Further, this method leads to a milder route to macromer synthesis consisting of 2-HEMA/PEGMA and an oligoester chain segment as compared to chemical routes. Unlike published chemical methods to synthesize such types of brush copolymers, this enzymatic method did not require dry conditions, exclusion of oxygen for polyester synthesis, or the use of highly reactive organometallic catalysts. Further, the use of Novozyme 435 as the biocatalyst (<2% water initiated chains) overcomes the limitations of possible homo-polyesters obtained using chemical catalysis.

Both 2-HEMA-*co*-b-PPDL and PEGMA-*co*-b-PPDL macromers are highly crystalline and thermally stable. The crystal phase is that of poly(pentadecalactone), PPDL, in all cases. A moderate decrease of crystallinity is observed upon radical polymerization of the macromers. This phenomenon arises from restricted mobility of the crystallizable pendant side chains by the polymethacrylate backbone. The particularly high crystal phase content of PEGMA-*co*-b-PPDL and P(PEGMA-*co*-b-PPDL) is attributed to the incorporation of PEG segments in extended zigzag conformation into the PPDL crystal lattice.

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Supporting Information Available: Spectra of products from Novozym 435-catalyzed ring-opening polymerization of PDL at 70 °C in toluene using PEGMA as initiator. This material is available free of charge via the Internet at http://pubs.acs.org.

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