Macromolecules

Volume 15, Number 2 March–April 1982

Synthesis and Polymerization of Pentaerythritol Acrylate and Methacrylate and Their Bicyclic Ortho Esters

Anne Buyle Padías and H. K. Hall, Jr.*

Chemistry Department, University of Arizona, Tucson, Arizona 85721.
Received May 7, 1981

ABSTRACT: Pentaerythritol (1) was converted to pure pentaerythritol acrylate (7) or pentaerythritol methacrylate (15) by using a bicyclic ortho ester to protect three of the hydroxyl groups. Monomer 7 was synthesized in two ways. Tetrol 1 was converted by triethyl orthoformate to 4-(hydroxymethyl)-2,6,7-trioxabicyclo[2.2.2]octane (2). Esterification with acryloyl chloride gave 4-(acryloxymethyl)-2,6,7-trioxabicyclo[2.2.2]octane (5), hydrolysis of which gave 7. Alternatively, bromopentaerythritol (3), prepared from 1 by an improved procedure, was converted to its ortho ester 4 and then by cuprous acrylate to 5 in good yield. Monomer 15 was synthesized similarly by using methacryloyl chloride. Attempted isolation of 15 led to premature polymerization. Monomer 7 was obtained as an extremely viscous material. Free radical polymerization of 7 gave the corresponding water-soluble polymer 10 in reasonably high molecular weight. Attempted isolation of 10 led to insolubilization. Free radical homopolymerization of bicyclic acrylate 5 and methacrylate 11 gave soluble homopolymer only in sulfolane; hydrolysis of the former polymer gave 10 in lower molecular weight. Copolymers of 5 and 11 with vinyl monomers were also synthesized.

Introduction

Interest in water-soluble polymers is currently high because of their potential as flocculants, biopolymer analogues, etc. Two abundant commercial chemicals, pentaerythritol and acrylic acid, are water soluble. However, the potential monomer pentaerythritol acrylate has not been isolated and identified (although multifunctional pentaerythritol acrylates are used commercially in cross-linking applications).

Pentaerythritol, 2,2-bis(hydroxymethyl)-1,3-propanediol, is not expected to give exclusively the monoacrylate when esterified with 1 equiv of acrylic acid by conventional methods. The four hydroxyl groups are equally reactive in principle, and multifunctional acrylates will be formed. The presence of even traces of these polyacrylates will result in cross-linked polymers. Therefore, we planned to protect three of the hydroxyl groups as a bicyclic ortho ester group before forming the acrylate derivative.

Bicyclic ortho esters were first synthesized in very low yield by Crank and Eastwood[1] and much more successfully by Hall and De Blauwe[2-5] by reacting the respective triols with triethyl orthoformate in dibutyl or dioctyl phthalate, with removal under vacuum of the very reactive bicyclic ortho esters as formed to prevent oligomerization.

Results

Monomer Syntheses. 4-(Acryloxymethyl)-2,6,7-trioxabicyclo[2.2.2]octane (5) via the 4-Hydroxymethyl Derivative 2. 4-(Hydroxymethyl)-2,6,7-trioxabicyclo[2.2.2]octane (2) was synthesized from equimolar amounts of pentaerythritol and triethyl orthoformate in dioctyl phthalate in the presence of a trace of *p*-toluenesulfonic acid. This method has been described in our previous papers.[2-5] This compound though required much more severe conditions than those previously used (195 vs. 140 °C at 0.5 mmHg). To prevent oligomerization the condenser was chilled to −50 °C. Yields were variable and the extreme conditions made these experiments somewhat difficult.

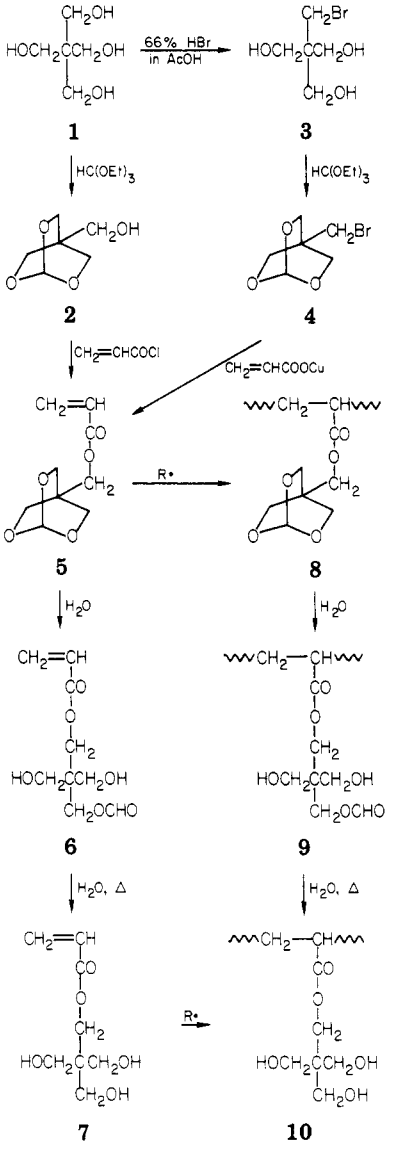
Esterification of the obtained alcohol 2 with acryloyl chloride resulted in 4-(acryloxymethyl)-2,6,7-trioxabicyclo[2.2.2]octane (5) in good yield (Scheme I).

4-(Acryloxymethyl)-2,6,7-trioxabicyclo[2.2.2]octane (5) via the 4-Bromomethyl Derivative 4. As a more convenient alternate route, pentaerythritol was converted to bromopentaerythritol (3). The bicyclic ortho ester 4 formed very easily by reacting bromopentaerythritol with triethyl orthoformate in the presence of a trace of *p*-toluenesulfonic acid in dioctyl phthalate at about 140 °C under vacuum in a large sublimation apparatus. The 4-(bromomethyl)-2,6,7-trioxabicyclo[2.2.2]octane (4) collected on the cold finger. A yield of up to 65% could be obtained and the reaction scale could be adjusted to handle 20 g of bromopentaerythritol, a limit determined only by the size of the available apparatus. This and all other 2,6,7-trioxabicyclo[2.2.2]octanes encountered were highly crystalline solids.

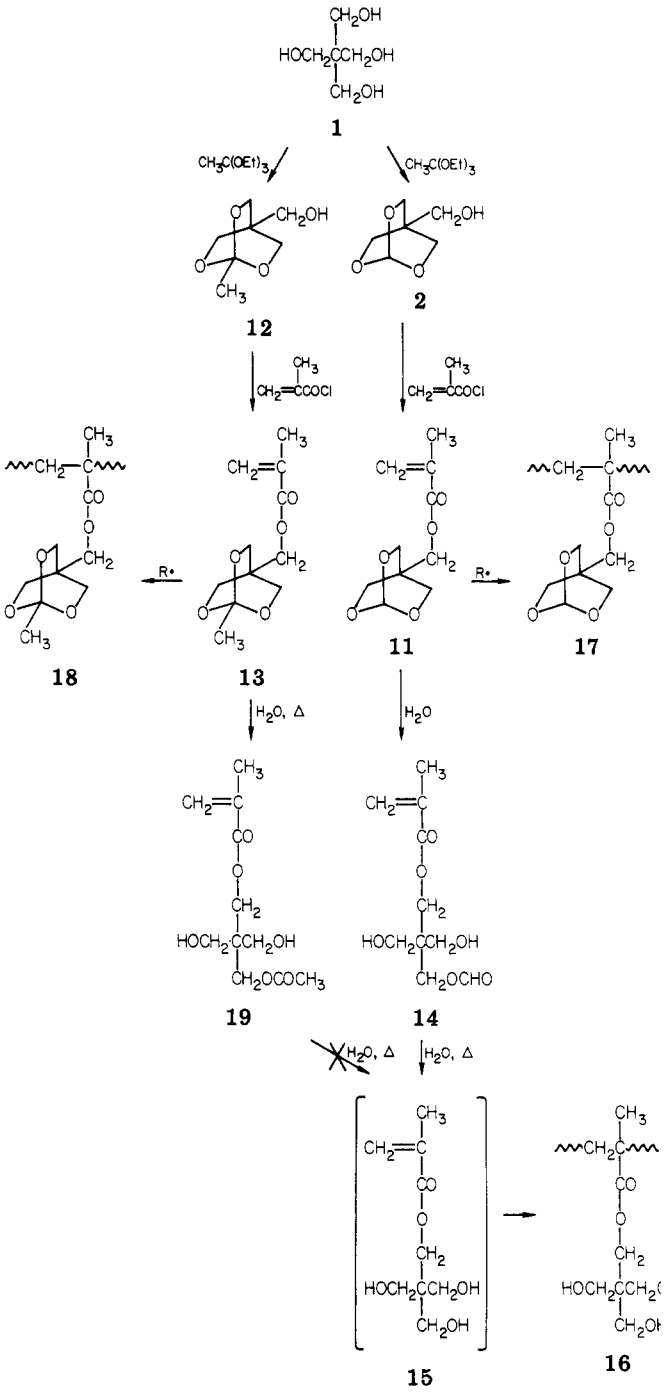
The bromo derivative 4 was treated with cuprous acrylate to obtain 4-(acryloxymethyl)-2,6,7-trioxabicyclo-[2.2.2]octane (5) in one step. The required cuprous acry-

0024-9297/82/2215-0217$01.25/0

Scheme I
Acrylate Monomers and Polymers via Bicyclic Orthoformates



Scheme II
Methacrylate Monomers and Polymers via Bicyclic Orthoformate and Orthoacetate



late was obtained by an improved procedure: reaction of cupric carbonate with acrylic acid in acetonitrile to form cupric acrylate and subsequent reduction with copper metal in acetonitrile in the presence of acrylic acid, inhibitor, and molecular sieves. The white cuprous acrylate was very sensitive to air and was immediately reacted with **4** in pyridine. 4-(Acryloxymethyl)-2,6,7-trioxabicyclo-[2.2.2]octane (**5**) was obtained as white needles in good yield (60%). It was identical with the material described above (Scheme I).

Pentaerythritol Acrylate (7). Compound **7** could be obtained by hydrolysis of 4-(acryloxymethyl)-2,6,7-trioxabicyclo[2.2.2]octane (**5**) in water. One-half hour after mixing, complete dissolution had taken place; NMR spectroscopy showed that formate **6** was obtained. To selectively hydrolyze the formate ester, the water solution was heated to 70 °C for several hours.

Pentaerythritol acrylate (**7**), obtained after evaporation of the water and drying, showed remarkable behavior. NMR and IR spectra indicated that indeed monomeric pentaerythritol acrylate (**7**) had been obtained. Yet the product had the appearance of a glue and could be pulled into a fiber 1 m long. This monomer has not been obtained in crystalline form.

4-(Methacryloxymethyl)-2,6,7-trioxabicyclo[2.2.2]-octane (11). 4-(Methacryloxymethyl)-2,6,7-trioxabicyclo[2.2.2]octane (**11**) was synthesized by reacting 4-(hydroxymethyl)-2,6,7-trioxabicyclo[2.2.2]octane (**2**) with methacryloyl chloride as described for the acrylate derivative **5** (see Scheme II).

1-Methyl-4-(methacryloxymethyl)-2,6,7-trioxabicyclo[2.2.2]octane (13). The bicyclic orthoacetate derivative of pentaerythritol, 1-methyl-4-(hydroxymethyl)-2,6,7-trioxabicyclo[2.2.2]octane (**12**), was also prepared. Its methacrylate derivative **13** was prepared as described for the bicyclic orthoformate (Scheme II).

Pentaerythritol Methacrylate (15). In contact with water the bicyclic orthoformate **11** slowly hydrolyzed to the formate ester **14** and then, at higher temperature, complete hydrolysis occurred to pentaerythritol meth-

Table I
Polymerization of Pentaerythritol Acrylate (7)

wt of monomer 7, mg	amt of initiator $K_2S_2O_8$		amt of $Na_2S_2O_3$		total volume, mL	method [a]	η_{inh}, [b] dL·g^{-1}	remarks
	mg	mol %	mg	mol %				
250	5	1.5			4	UV/45 °C		contains gel
250	5	1.5			4	80 °C		contains gel
190	5	2			10	UV/45 °C	c	viscous
380	5	1			10	UV/45 °C	0.25	
190	0.25	0.1			2	UV/45 °C	0.79	
190	0.12	0.025			2	UV/45 °C	0.57	
190	5	1	5	2	2	25 °C	0.45	
190	0.5	0.1	0.5	0.2	2	25 °C	0.49	
190	0.25	0.05	0.25	0.1	2	25 °C	0.96	

[a] All polymerizations were run for 16 h with stirring except for the first two; all runs went to 100%. [b] Viscosities were measured in an Ostwald viscosimeter, using water as solvent, at 30 °C. Solutions were diluted to 10 mL. [c] Polymers were isolated and impossible to redissolve.

Table II
Homopolymerization of 4-(Acryloxymethyl)- (5), 4-(Methacryloxymethyl)- (11), and 1-Methyl-4-(methacryloxymethyl)-2,6,7-trioxabicyclo[2.2.2]octane (13)

monomer	time, [a] h	amt of initiator, mol %	solvent	polymer	yield, %	η_{inh}, dL·g^{-1}	remarks
5	20	1 [b]	benzene	8	90		not soluble (gel)
5	20	1	acetone	8	?		not soluble (solid)
5	8	1	benzene	8	10		not soluble
5	20	1	benzene	8	90		not soluble (gel)
5	20 [c]	1	benzene	8	85		not soluble
5	16	1	hexafluoro-2-propanol	8	100		soluble, partially decomposed by acidic solvent
5	16	1	sulfolane	8	98	0.2 [d]	viscosity measured without prior isolation
5	16	0.5	sulfolane	8	100	0.2 [d]	viscosity measured without prior isolation
11	20	5	benzene	17	30		not soluble
11	20	5	sulfolane	17	75	0.92 [e]	soluble
13	20	1	benzene	18	87	0.82 [e]	not soluble
13	20	3	benzene	18	95	0.52 [e]	not soluble
13	20	3	hexafluoro-2-propanol	18	68		soluble, partially decomposed by acidic solvent

[a] Conditions: UV, 40 °C except as noted; AIBN initiator except as noted. [b] Benzoyl peroxide initiator. [c] 80 °C, no UV. [d] Inherent viscosity was measured in an Ostwald viscosimeter in sulfolane at 30 °C. [e] Inherent viscosity in hexafluoro-2-propanol at 30 °C.

acrylate (15). Attempts to isolate 15 were unsuccessful. The monomer polymerized to poly(pentaerythritol methacrylate) (16).

The bicyclic orthoacetate 13 in the presence of water hydrolyzed to the acetate 19, which was very stable and did not hydrolyze further.

Polymerization. Homopolymerization of Pentaerythritol Acrylate (7) and Methacrylate (15). Polymerization of 7 performed in water without magnetic stirring, using potassium persulfate as initiator, under UV light at about 45 °C, or at 80 °C, resulted in gel formation. If the polymerization mixture was stirred during the reaction, poly(pentaerythritol acrylate) (10) stayed in solution. The polymerization was also carried out at room temperature using a redox system as initiator. Potassium persulfate and sodium thiosulfate were mixed in the presence of monomer after degassing. The solutions were visibly viscous after 2 h, but the polymerization was allowed to proceed for 16 h.

All polymerizations went to 100% as shown by NMR spectroscopy. Polymer 10 was freeze-dried, which resulted in a brittle, glassy solid. The polymer swelled but was no longer soluble in water after drying. The viscosities were subsequently measured immediately by diluting the solutions obtained from the polymerizations without isolation. Poly(pentaerythritol acrylate) (10) of high molecular weight was obtained at low initiator concentrations. The results of these polymerizations are summarized in Table I.

Pentaerythritol methacrylate (15) spontaneously polymerized during isolation. The structure of poly(pentaerythritol methacrylate) (16) was confirmed by NMR and IR spectroscopy.

Homopolymerization of Bicyclic Ortho Esters 5, 11, and 13 (Table II). 4-(Acryloxymethyl)-2,6,7-trioxabicyclo[2.2.2]octane (5) was polymerized under the influence of radical initiators. In most cases polymer 8 precipitated from solution, except when sulfolane or hexafluoro-2-propanol was used as solvent. But even when these solvents were used, isolated polymer 8 would not completely redissolve. Accordingly, polymer 8 was characterized by the viscosity of its sulfolane solution directly prepared by polymerization. Moderate inherent viscosities were observed.

4-(Methacryloxymethyl)-2,6,7-trioxabicyclo[2.2.2]octane (11) was polymerized radically in benzene and sulfolane to 17. The yields were lower than observed for the acrylate. Polymer 17 precipitated from benzene but was soluble in sulfolane and dimethyl sulfoxide.

1-Methyl-4-(methacryloxymethyl)-2,6,7-trioxabicyclo-[2.2.2]octane (13) polymerized radically in benzene to 18 but precipitated out of solution. Polymerization in hex-

Table III
Bulk Copolymerizations of 4-(Acryloxymethyl)-2,6,7-trioxabicyclo[2.2.2]octane (5) (M_1) with Vinyl Monomers (M_2)[a]

amt of M_1, mg	comonomer M_2	amt of comonomer, mg	M_1/M_2 mole ratio	yield, mg	mole ratio in polymer
200	methyl acrylate	42	66/33	120 (49%)	45/55
200	methyl acrylate	86	50/50	275 (96%)	40/60
200	methyl methacrylate	50	66/33	221 (88%)	56/44
200	methyl methacrylate	100	50/50	252 (84%)	41/59
200	*p*-methoxystyrene	67	66/33	113 (45%)	50/50
200	*p*-methoxystyrene	135	50/50	149 (49%)	40/60

[a] Polymerization catalyst: 1 mol % of AIBN. Polymerization conditions: UV light at 40 °C for 16 h.

afluoro-2-propanol gave soluble polymer, but the IR spectrum indicated that decomposition of the bicyclic orthoacetate ring had occurred (strong carbonyl and hydroxyl bands). All the above polymers show great diffraction under a polarizing filter.

Hydrolysis of Poly[4-(acryloxymethyl)-2,6,7-trioxabicyclo[2.2.2]octane] (8) to Poly(pentaerythritol acrylate) (10). Poly[4-(acryloxymethyl)-2,6,7-trioxabicyclo[2.2.2]octane] (8) was hydrolyzed in water to obtain poly(pentaerythritol acrylate) (10) (Scheme I). To dissolve polymer 8, the mixture had to be heated to 70 °C for 3 h. NMR spectroscopy showed that, here also, partial hydrolysis occurred from homopolymer 8 to polymer monoformate 9. After 2 weeks at room temperature the sample was again examined and complete hydrolysis had taken place to poly(pentaerythritol acrylate) (10). Because the inherent viscosities of the original polymer 8 were rather low, the resulting polymer 10 would have a rather low molecular weight, too. In fact, this route gave polymer of lower molecular weight than direct polymerization of monomeric pentaerythritol acrylate (7).

Copolymerization of 4-(Acryloxymethyl)-2,6,7-trioxabicyclo[2.2.2]octane (5) with Vinyl Monomers. 4-(Acryloxymethyl)-2,6,7-trioxabicyclo[2.2.2]octane (5) was copolymerized with a variety of vinyl monomers to increase the solubility of their polymers in organic solvents. As comonomers, methyl acrylate, methyl methacrylate, and *p*-methoxystyrene were used. The results are summarized in Table III.

All copolymers showed good incorporation of 4-(acryloxymethyl)-2,6,7-trioxabicyclo[2.2.2]octane. The composition of the copolymers was determined by NMR spectroscopy. They were all white powders and were soluble in chloroform and insoluble in benzene. The methyl methacrylate copolymers were very soluble and showed good incorporation. The methyl acrylate copolymers were not soluble. The *p*-methoxystyrene copolymers were obtained in lower yields (about 50%) and were very soluble. Attempts to hydrolyze the ortho ester links in the copolymers in aqueous acidic media failed.

Discussion

Monomer Synthesis. The Hall–De Blauwe method for synthesizing bicyclic ortho esters proved useful in synthesizing 4-(hydroxymethyl)-2,6,7-trioxabicyclo[2.2.2]octane (2), but more extreme temperatures were required in this case. The high temperature (195 °C) was required to remove the monomer as formed, probably because the hydroxymethyl group confers a high boiling and sublimation temperature to the ortho ester structure. Oligomerization on the surrounding warm surfaces was a problem and was the main reason for inconsistent yields.

The bicyclic orthoacetate 12 was synthesized because it is more stable under the forcing conditions used in these reactions. This fact is corroborated by a paper by Endo, Saigo, and Bailey[6] published during the course of this work. These workers were able to synthesize the bicyclic orthopropionate starting from triethyl orthopropionate and pentaerythritol in high yield. Hydroxymethyl bicyclic ortho esters 2 and 12 were then easily converted to acrylate 5 and methacrylates 11 and 13 by using the corresponding acid chlorides.

The alternate synthesis route involves 4-(bromomethyl)-2,6,7-trioxabicyclo[2.2.2]octane (4) as an intermediate. To obtain this compound, pentaerythritol (1) was first converted to bromopentaerythritol (3) by a procedure much improved over the literature procedure.[7] The authors of the literature procedure report yields up to 55%. The yields obtained in our laboratory were less than 20% with this method. The method was improved by increasing the hydrobromic acid concentration from 48% to 66%. The product was then purified by taking advantage of differences in solubility of the starting material and the products formed. The bromomethyl bicyclic ortho ester 4 was easily obtained in high yield by reaction of bromopentaerythritol and triethyl orthoformate and was converted to monoacrylate with cuprous acrylate. Lewis and Goldberg[8] and Klumpp et al.[9] had reported that cuprous carboxylates in pyridine reacted with various organic bromides to give the corresponding carboxylate esters. Even vinyl and neopentyl bromides gave the corresponding acetates under these conditions. We synthesized the extremely air-sensitive cuprous acrylate in a manner analogous to that described for cuprous acetate by Edwards and Richards.[11] This reagent converted bicyclic bromo ortho ester 4 smoothly to the corresponding acrylate 5 in a 60% yield. Incidentally, the success of this reaction with a neopentyl bromide derivative makes it likely that this reagent may find use in the synthesis of other difficultly accessible acrylates.

Hydrolysis of 4-(acryloxymethyl)-2,6,7-trioxabicyclo[2.2.2]octane (5) in hot water led to the desired pentaerythritol acrylate (7). Cold water rapidly hydrolyzed the bicyclic orthoformate to the formate 6. Higher temperatures were required to hydrolyze the formate group; these conditions did not affect the more stable acrylate ester function in the molecule.

In the methacrylate series (Scheme II) both the bicyclic orthoformate 11 and the orthoacetate 13 were synthesized. The hydrolysis of 4-(methacryloxymethyl)-2,6,7-trioxabicyclo[2.2.2]octane (11) proceeded in the same way as described for the acrylate derivative. Pentaerythritol methacrylate (15) was obtained and characterized in water solution. Attempts to isolate 15 though resulted in spontaneous polymerization. This polymethacrylate derivative 16 was characterized by NMR and IR. On the other hand, 1-methyl-4-(methacryloxymethyl)-2,6,7-trioxabicyclo[2.2.2]octane (13) in hot water yielded the acetate 17 and could not be completely hydrolyzed to pentaerythritol methacrylate (15) without side reaction at the methacrylate ester function.

Polymerization. Pentaerythritol acrylate (7) was po-

lymerized radically in water. This was the only practical solvent, but the polymerization was accompanied by a tendency to form gel, both during polymerization and during attempted isolation of polymer **10**. The former was avoided by stirring the polymerization solution to ensure homogeneity and the latter by not isolating the polymer but characterizing it by NMR spectroscopy and by the viscosity of the as-polymerized solution. We are inclined to believe that facile ester alcoholysis between neighboring polymer chains accounts for the observed cross-linking and gelation. Nonetheless, reasonably high inherent viscosities were obtained in water solution.

The bicyclic ortho ester acrylate **5** and methacrylates **11** and **13** were polymerized radically through the vinyl function. The obtained homopolymers are insoluble in most organic solvents except sulfolane and hexafluoro-2-propanol. The high acidity of the latter though causes partial decomposition. As mentioned, all the 2,6,7-trioxabicyclo[2.2.2]octanes we have studied are crystalline and high melting (see also ref 5). These bicyclic substituents may convey some stereoregular structure to the polymer, which could explain the insolubility in most organic solvents. The acrylate polymer **8** is soluble in sulfolane but of relative low molecular weight as shown by the inherent viscosity. The methacrylate polymers **17** and **18** are of somewhat higher molecular weight.

The polyacrylate with the 2,6,7-trioxabicyclo[2.2.2]octane side groups (**8**) was hydrolyzed and the poly(pentaerythritol acrylate) (**10**) was obtained. Here also the hydrolysis occurred in two stages: the hydrolysis of the bicyclic structure to the formate **9** and the subsequent hydrolysis of this ester function to yield the third hydroxyl group. This reaction proceeded very slowly partly due to the insolubility of **8**. Because the polymers containing the bicyclic structure were only of low or moderate molecular weight, this route to poly(pentaerythritol acrylate) was not fully investigated.

To increase the wettability of common vinyl polymers, copolymers with **5** could be synthesized; the incorporated bicyclic ortho ester groups should easily hydrolyze to yield hydrophilic functions in the copolymer. Methyl acrylate, methyl methacrylate, and *p*-methoxystyrene were radically copolymerized with **5**. The resulting copolymers were more soluble in organic solvents and possessed somewhat higher molecular weight than the homopolymer of **5**. However, the hydrophobic groups repulsed the water and as such prevented the hydrolysis of the bicyclic ortho ester functions.

It is interesting to point out that these monomers contain both a function that polymerizes radically and another function that allows cationic polymerization. These two routes lead to two entirely different polymers. The cationic polymerization of 2,6,7-trioxabicyclo[2.2.2]octane derivatives is extensively described in ref 5.

Experimental Section

Instrumentation. ^{1}H NMR spectra were obtained with Varian T-60 and EM-360L spectrometers. Infrared spectra were recorded with a Perkin-Elmer 710A spectrometer. Elemental analyses were performed by the University of Arizona Analytical Center (Tucson, Ariz.). Melting points were determined in a Thomas-Hoover melting point apparatus. All melting points and boiling points are uncorrected.

4-(Hydroxymethyl)-2,6,7-trioxabicyclo[2.2.2]octane (2). In a large sublimation apparatus equipped with a side arm for distillation of volatile material are mixed 6.8 g (0.05 mol) of pentaerythritol, 7.4 g (0.05 mol) of triethyl orthoformate, 150 mL of dioctyl phthalate, and a trace of anhydrous *p*-toluenesulfonic acid. Vigorous magnetic stirring is begun and the sublimator is immersed in an oil bath at 140 °C. After 2.5 mol equiv of ethanol has been collected, the bath temperature is raised to 195 °C, vacuum is applied to the apparatus (0.05 mmHg) and the cold finger is cooled with a methanol–dry ice mixture to about −50 °C. After about 15 min, crystals have collected on the cold finger, the DOP solution has cleared, and some DOP has distilled. At this point, the reaction is stopped. The crystals are washed with hexane to remove DOP and dissolved in chloroform, leaving behind any polymer formed. In a similar manner, an additional crop of crystals can be recovered from the distilled DOP. The alcohol is recrystallized from benzene, avoiding prolonged heating: yield 3.6 g (50%); mp 87–88 °C; NMR ($CDCl_3$) δ 5.5 (s, 1 H), 4.0 (s, 6 H), 3.4 (s, 2 H), 2.15 (s, 1 H); IR (KBr) 3350, 2970, 1560, 1470, 1380, 1150, 1050, 980, 910, 850, 750 cm^{-1}. Anal. Calcd: C, 49.31; H, 6.85. Found: C, 49.30; H, 6.80.

4-(Acryloxymethyl)-2,6,7-trioxabicyclo[2.2.2]octane (5). 4-(Hydroxymethyl)-2,6,7-trioxabicyclo[2.2.2]octane (**2**) (4.2 g, 30 mmol) is dissolved in 30 mL of dry tetrahydrofuran in the presence of a trace of 3,5-di-*tert*-butylcatechol and 30 mL (0.3 mmol) of dry triethylamine at 0 °C. Acryloyl chloride (2.7 g, 30 mmol) dissolved in 10 mL of tetrahydrofuran is added slowly. The mixture is stirred for an additional hour. The precipitate is filtered and the solvent is evaporated. The residue is dissolved in chloroform and the solution is passed through a silica gel column to remove residual triethylamine hydrochloride, which causes polymerization in attempts to recrystallize the acrylate. The product is recrystallized from hexane: yield 3.0 g (53%); mp 86–87 °C; NMR ($CDCl_3$) δ 6.4–5.8 (m, 3 H), 5.55 (s, 1 H), 4.0 (2 s, 8 H); IR (KBr) 3030, 2900, 1720, 1620, 1460, 1420, 1300, 1160, 1080, 1040, 1000, 935, 900, 860, 820 cm^{-1}. Anal. Calcd: C, 54.0; H, 6.0. Found: C, 53.9; H, 6.1.

Bromopentaerythritol (3). In a 2-L, three-necked flask equipped with a reflux condenser and an addition funnel are placed 200 g (1.47 mol) of pentaerythritol and 16 mL of 48% hydrobromic acid in about 500 mL of glacial acetic acid. The mixture is refluxed for ~0.5 h until all pentaerythritol is dissolved. Then 170 mL of 48% hydrobromic acid is added, followed by 310 mL of acetic anhydride, and the mixture is refluxed for 3 h. Then 94 mL of 48% hydrobromic acid followed by 150 mL of acetic anhydride is added and the mixture is refluxed for an additional 3 h. The acetic acid is then removed as completely as possible on a rotary evaporator. Ethanol (95%, 750 mL) and 17 mL of 48% hydrobromic acid are then added to the residue. The flask is equipped with a 1-m Vigreux column and the ethyl acetate/ethanol azeotrope is slowly distilled. When 500 mL of distillate has been collected, an additional 750 mL of 95% ethanol is added and the distillation is continued until about 400 mL remains. After cooling, the precipitated pentaerythritol is filtered. The solvent is evaporated and the residue is dissolved in water. The aqueous phase is extracted twice with carbon tetrachloride and twice with ether. The water is evaporated on the rotary evaporator and the last traces of water are removed by azeotropic distillation with toluene using a Dean–Stark trap. The solid is recrystallized from chloroform containing 10% acetonitrile. The first crop yielded 190 g of bromopentaerythritol. The total yield is 70%.

Bromopentaerythritol is very slightly soluble in chloroform, very soluble in ethanol, *sec*-butyl alcohol, and acetonitrile, and insoluble in ether: mp 72 °C (lit. mp 76 °C); NMR (CF_3COOH) δ 3.5 (s, 1 H), 4.0 (s, 3 H); IR (KBr) 3550 (br), 2920, 2870, 1450, 1240, 1190, 1120, 1020, 870, 840 cm^{-1}. Anal. Calcd: C, 30.15; H, 5.53. Found: C, 30.20; H, 5.37.

4-(Bromomethyl)-2,6,7-trioxabicyclo[2.2.2]octane (4). Bromopentaerythritol (**3**) (10 g, 0.05 mol) and 9 mL (0.05 mol) of triethyl orthoformate are mixed in a sublimation apparatus equipped with a side arm. The mixture is heated to about 100 °C with magnetic stirring, and 1.5 equiv of ethanol is allowed to distill. Then about 100 mL of dioctyl phthalate and a trace of anhydrous *p*-toluenesulfonic acid are added. Under vacuum the mixture is heated to about 140–150 °C. Periodically the collected crystals are removed from the cold finger. After about 3 h no more compound sublimes: yield 6.5 g (60%); mp 83–90 °C; NMR ($CDCl_3$) δ 3.15 (s, 2 H), 4.05 (s, 6 H), 5.6 (s, 1 H); IR (KBr) 3020, 2925, 2870, 1480, 1440, 1380, 1360, 1285, 1245, 1150 cm^{-1}. Anal. Calcd: C, 34.45; H, 4.31. Found: C, 34.60; H, 4.37.

Cuprous Acrylate. Cupric acrylate (12 g, 0.058 mol) is mixed with about 250 mL of dry acetonitrile, 30 g (0.5 mol) of copper foil, 5 mL of acrylic acid, a few molecular sieves, and a trace of 2,5-di-*tert*-butylcatechol. The reaction mixture is stirred for 24 h under nitrogen until all the blue color disappears. Some white precipitate is formed. The precipitate and the solution are decanted from the remaining copper in a glovebag under nitrogen and added to approximately 600 mL of dry ether. The white precipitate is filtered and dried, still under nitrogen; yield 12.6 g (81%).

4-(Acryloxymethyl)-2,6,7-trioxabicyclo[2.2.2]octane (5). Cuprous acrylate (10.7 g, 0.08 mol) and 4-(bromomethyl)-2,6,7-trioxabicyclo[2.2.2]octane (**3**) (12.5 g, 0.06 mol) are dissolved in 100 mL of dry pyridine under nitrogen. Some 2,5-di-*tert*-butylcatechol is added. The mixture is refluxed for 3 h. The pyridine is completely evaporated. The green solids are ground and placed in a Soxhlet extractor for extraction with hexane for 24 h. The hexane is evaporated and the solids are dissolved in chloroform. The solution is passed through a short silica gel column to remove any remaining copper salts. The acrylate is recrystallized from hexane. Long white needles are obtained: yield 6 g (60%); mp 86–87 °C.

Pentaerythritol Acrylate (7). 4-(Acryloxymethyl)-2,6,7-trioxabicyclo[2.2.2]octane (**5**) (3 g) is mixed with 30 mL of distilled water at room temperature. The mixture becomes homogeneous after 0.5 h. The NMR spectrum shows the presence of two methylene groups next to an ester group (δ 4.0) and two next to an alcohol (δ 3.5), which indicates only partial hydrolysis has taken place to formate **6**; NMR (D_2O) δ 8 (s, 1 H), 6.4–5.8 (m, 3 H), 4.5 (H_2O), 4.0 (2 s, 4 H), 3.5 (s, 4 H).

The reaction mixture is then heated to 70 °C. The NMR spectrum of the reaction mixture is checked periodically to follow the reaction. After 4.5 h the reaction is complete. The water and formed formic acid are evaporated and the reaction product is dried under vacuum. A gluelike material is obtained which does not crystallize after 3 days at −10 °C. The material can be pulled into fibers 1 m long. The pentaerythritol acrylate is insoluble in all organic solvents, including chloroform and acetonitrile. It is soluble in water: NMR (D_2O) δ 6.2–5.7 (m, 3 H), 4.5 (H_2O), 3.95 (s, 2 H), 3.45 (s, 6 H); IR (KBr) 3400, 2950, 2890, 1710, 1630, 1610, 1470, 1410, 1300, 1200, 1040, 820 cm^{-1}.

4-(Methacryloxymethyl)-2,6,7-trioxabicyclo[2.2.2]octane (11). The procedure is identical with that described for the acrylate derivative, except that methacryloyl chloride is used in place of acryloyl chloride: yield 45%; mp 89–91 °C; NMR ($CDCl_3$) δ 6.2 (m, 1 H), 5.7 (m, 1 H), 5.6 (s, 1 H), 4.1 (s, 6 H), 4.0 (s, 2 H), 2.0 (d, 3 H); IR (KBr) 2970, 2900, 1700, 1630, 1460, 1380, 1330, 1160, 1000, 930, 860 cm^{-1}. Anal. Calcd: C, 56.0; H, 6.5. Found: C, 56.0; H, 6.5.

Pentaerythritol Methacrylate (15). 4-(Methacryloxymethyl)-2,6,7-trioxabicyclo[2.2.2]octane (**11**) (30 mg) is mixed with 1 mL of D_2O. After 2 h at 60 °C dissolution occurs and the NMR spectrum indicates partial hydrolysis to the formate **14** (two CH_2COO at δ 4.4 and 4.3 and two CH_2OH at δ 3.8); NMR (D_2O) δ 6.2 (m, 1 H), 5.8 (m, 1 H), 4.4 (s, 2 H), 4.3 (s, 2 H), 3.8 (s, 4 H), 2.0 (d, 3 H). After 20 h at 60 °C, complete hydrolysis occurs to pentaerythritol methacrylate. Attempts to isolate **15** resulted in polymerization; NMR (D_2O) δ 6.2 (m, 1 H), 5.8 (m, 1 H), 4.2 (s, 2 H), 3.7 (s, 6 H), 2.0 (d, 3 H).

1-Methyl-4-(hydroxymethyl)-2,6,7-trioxabicyclo[2.2.2]octane (12). Pentaerythritol (13.6 g, 0.1 mol), triethyl orthoacetate (16 g, 0.1 mol), a trace of *p*-toluenesulfonic acid, and 100 mL of dioctyl phthalate are mixed at 140 °C in a distillation apparatus. After the theoretical amount of ethanol has distilled, the temperature is raised to 180–190 °C and the pressure is reduced to <0.5 mmHg. White product crystallizes on the condenser and is recrystallized from benzene: yield 8.0 g (50%); mp 112 °C; NMR ($CDCl_3$) δ 4.0 (s, 6 H), 3.4 (d, 2 H), 2.3 (t, 1 H), 1.4 (s, 3 H); IR (KBr) 3400, 2950, 2890, 2770, 1380, 1300, 1140, 1050, 850 cm^{-1}. Anal. Calcd: C, 52.5; H, 7.5. Found: C, 52.3; H, 7.3.

1-Methyl-4-(methacryloxymethyl)-2,6,7-trioxabicyclo[2.2.2]octane (13). Methacryloyl chloride (6.0 g, 0.06 mol) in 200 mL of tetrahydrofuran is slowly added to a flask containing 9.0 g (0.06 mol) of **12**, 60 mL (0.6 mol) of triethylamine, and a trace of 3,5-di-*tert*-butylcatechol in 50 mL of tetrahydrofuran at 0 °C. The mixture is stirred for 1 h, the precipitate is filtered, and the solvent is evaporated. The residue dissolved in chloroform is passed through a silica gel column and recrystallized from hexane: yield 5.4 g (40%); mp 86 °C; NMR ($CDCl_3$) δ 6.1 (m, 1 H), 5.6 (m, 1 H), 4.0 (s, 6 H), 3.9 (s, 2 H), 1.9 (m, 3 H), 1.4 (s, 3 H); IR (KBr) 2950, 2890, 2780, 1720, 1600 cm^{-1}. Anal. Calcd: C, 57.9; H, 7.0. Found: C, 57.7; H, 7.0.

Hydrolysis of 1-Methyl-4-(methacryloxymethyl)-2,6,7-trioxabicyclo[2.2.2]octane (13). Deuterium oxide (1 mL) is mixed with **13** (50 mg). After 2 h, dissolution occurs, and the resulting solution contains the partially hydrolyzed product **16** (two CH_2COO at δ 4.1 and 4.05 and two CH_2OH at δ 3.55); NMR (D_2O) δ 6.1 (m, 1 H), 5.6 (m, 1 H), 4.1 (s, 2 H), 4.05 (s, 2 H), 3.55 (s, 4 H), 2.0 (s, 3 H), 1.8 (m, 3 H). This acetate **16** does not hydrolyze further to pentaerythritol methacrylate (**15**) even at higher temperature. Addition of acid results in decomposition of the material.

Polymerization of 4-(Acryloxymethyl)-2,6,7-trioxabicyclo[2.2.2]octane (5). Benzene was dried over sodium and distilled just before use. Acetone was refluxed over potassium permanganate, distilled, and redistilled over calcium hydride. Hexafluoro-2-propanol was distilled from calcium hydride. Monomer **5**, appropriate comonomer in the copolymerizations, initiator, and solvent are mixed in an ampule, cooled to −78 °C, degassed, thawed, cooled, and degassed again. Then the ampule is sealed. The polymerization conditions for each run are specified in the tables. At the end of the polymerization, attempts are made to dissolve the polymer, and the whole is precipitated in hexane. The polymer is filtered, dried, and weighed: NMR (Me_2SO-d_6) δ 5.5 (s, 1 H), 3.9 (s, 8 H), 2.3–1.0 (2 broad signals, 3 H); IR (KBr) 2940, 2880, 1730, 1470, 1370, 1150, 1040, 1000, 920, 860 cm^{-1}. Anal. Calcd: C, 53.6; H, 5.4. Found: C, 53.3; H, 5.6.

Hydrolysis to Poly(pentaerythritol Acrylate) (10). Poly[4-(acryloxymethyl)-2,6,7-trioxabicyclo[2.2.2]octane] (**8**) (50 mg) was mixed with 1 mL of deuterated water in an NMR tube with 4 mol % of formic acid. The heterogeneous mixture was heated to 70 °C for 3 h until homogeneous. The NMR spectrum indicates only partial hydrolysis has occured to structure **9** (two CH_2COO at δ 4.5 and two CH_2OH at δ 3.3); NMR (D_2O) δ 8.3 (s, 1 H), 5 (H_2O), 4.5 (br s, 4 H), 3.3 (br s, 4 H). After 2 weeks at room temperature the following NMR spectrum indicated that complete hydrolysis had taken place to poly(pentaerythritol acrylate) (**10**): NMR (D_2O) δ 7.5 (HCOOH, 1 H), 3.4 (s, 2 H), 2.9 (s, 6 H), 1.8–0.9 (m, 3 H).

Polymerization of 4-(Methacryloxymethyl)-2,6,7-trioxabicyclo[2.2.2]octane (11) and 1-Methyl-4-(methacryloxymethyl)-2,6,7-trioxabicyclo[2.2.2]octane (13). The polymerization is carried out as described above for **5**.

For **11**, the hexane-insoluble polymer is soluble in dimethyl sulfoxide: NMR (Me_2SO-d_6) δ 5.6 (s, 1 H), 4.0 (br s, 8 H), 2.2–1.4 (5 H); IR (KBr) 2950, 2900, 1730, 1470, 1380, 1160, 1040, 1000, 930, 860 cm^{-1}. Anal. Calcd: C, 56.1; H, 6.5. Found: C, 55.5; H, 6.8.

For **13**, the polymer is soluble in chloroform and acetone: NMR ($CDCl_3$) δ 4.0 (s), 3.8 (br peak), 2.2–0.5 (br peak), 1.5 (s); IR (KBr) 3500 (w), 2950, 2880, 1730 (w), 1475, 1400, 1360, 1300, 1130, 1060, 990, 860 cm^{-1}. Anal. Calcd: C, 57.9; H, 7.0. Found: C, 57.8; H, 7.0.

Polymerization of Pentaerythritol Acrylate (7). 4-(Acryloxymethyl)-2,6,7-trioxabicyclo[2.2.2]octane (1 g) is mixed with 10 mL of redistilled water. The bicyclic ortho ester is hydrolyzed to pentaerythritol acrylate (**7**) at 60 °C for 4 h. The only byproduct formed is formic acid, which does not interfere with the radical polymerization. The water solution is divided in several vials and initiator is added. When potassium persulfate and sodium thiosulfate were chosen as the initiating system, a Y-tube was used. The mixture is degassed twice and then the vials are sealed. The pentaerythritol acrylate is polymerized under the conditions described in Table I. For the measurement of the inherent viscosity, the solutions are diluted to 10 mL. The polymers are isolated by freeze-drying; NMR (D_2O) δ 3.4 (s, 2 H), 2.3 (s, 6 H), 2–0.9 (2 br s, 3 H). Anal. Calcd: C, 47.72; H, 6.87. Found: C, 47.90;, H, 6.72.

Acknowledgment. We are deeply indebted to the Celanese Research Co., particularly Dr. D. R. Wilson, for supporting this work.

References and Notes

(1) Crank, G.; Eastwood, F. W. *Aust. J. Chem.* **1964**, *17* (12), 1385.
(2) Hall, H. K., Jr.; Steuck, M. J. *J. Polym. Sci., Polym. Chem. Ed.* **1973**, *11*, 1035.
(3) Hall, H. K., Jr.; De Blauwe, F.; Pyriadi, T. *J. Am. Chem. Soc.* **1975**, *97*, 3954.
(4) Yokoyama, Y.; Padías, A. Buyle; De Blauwe, F.; Hall, H. K., Jr. *Macromolecules* **1980**, *13*, 352.
(5) Yokoyama, Y.; Padías, A. B.; Bratoeff, E. A.; Hall, H. K., Jr. *Macromolecules* **1982**, *15*, 11.
(6) Endo, T.; Saigo, K.; Bailey, W. J. *J. Polym. Sci., Polym. Lett. Ed.* **1980**, *18*, 457.
(7) Wawzonek, S.; Matar, A.; Issidoris, C. H. "Organic Syntheses"; Wiley: New York, 1963; Collect. Vol. IV, p 681.
(8) Lewin, A. H.; Goldberg, N. L. *Tetrahedron Lett.* **1972**, 491.
(9) Klumpp, G. W.; Bos, H.; Schakel, M.; Schmitz, R. F.; Vrielink, J. J. *Tetrahedron Lett.* **1975**, 3429.
(10) Ogura, T.; Fernando, Q. *Inorg. Chem.* **1973**, *12*, 2611.
(11) Edwards, D. A.; Richards, R. *J. Chem. Soc., Dalton Trans.* **1973**, 2463.

Syntheses of ABA Triblock Copolymers Initiated with Polymeric Metalloester

Toshimitsu Suzuki,* Osamu Yamada, Yoshimasa Murakami, Yoshinobu Takegami, and Yoshihisa Watanabe

Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto University, Kyoto 606, Japan.

Received October 7, 1981

ABSTRACT: Anionic polymerization of methyl methacrylate (MMA) and *tert*-butyl methacrylate (BMA) was initiated with lithiated polyoxirane diisobutyrate (PEDB, M_n = 1000 or 2700) in tetrahydrofuran (THF) or toluene. The resulting block copolymers were characterized by ^1H and ^{13}C NMR spectroscopy, gel permeation chromatography (GPC), and solvent extractions. The copolymers prepared in THF show unimodal and relatively narrow molecular weight distributions. Methanolysis of the block copolymer (M_n = 8700, center block M_n = 1000; unimodal and relatively narrow molecular weight distribution) followed by GPC analysis proved that the copolymer was a symmetric triblock copolymer. The stereosequence distributions of the polymethacrylate part in the copolymer appeared rich in syndiotactic triad when THF was used as a solvent or PEDB-4000 (M_n = 2700) was used as an initiator in toluene. An isotactic block of PMMA was obtained when PEDB-1000 was used as an initiator in toluene.

Introduction

Recently, block copolymers containing hydrophobic and hydrophilic blocks have received much attention from the biomedical point of view. Polyoxirane, which is commonly named poly(ethylene glycol), is one of the common hydrophilic groups studied.

In our previous papers,[1,2] we studied the preparation of hydrophobic–hydrophilic–hydrophobic ABA-type triblock copolymer. Block copolymers were synthesized by the polymerization of methyl methacrylate (MMA) initiated with the disodium salt of polyoxirane (PEO) in the presence of a crown ether or a cryptate. However, a transesterification reaction between PEO and the methoxy group in MMA was accompanied by polymerization, resulting in a PEO grafted block copolymer. Subsequently, we developed a benzylamino derivative of PEO (PEO-N) as an alternative initiator system for the polymerization of MMA.[1,3] The initiation with disodium or dilithium amide of PEO-N resulted in a PMMA–PEO–PMMA triblock copolymer having a unimodal and relatively narrow molecular weight distribution, but it was very difficult to obtain diamine derivatives of PEO having higher molecular weights quantitatively.

Rathke et al. found that the α positions of acetic acid esters were easily, almost quantitatively lithiated by the use of lithium bis(tetramethylsilyl)amide or lithium dialkylamide;[4,5] a further advance was reported by Lochmann et al., who initiated polymerization of MMA with the growing-end-like anion obtained by α-lithiation of methyl isobutyrate using lithium diisopropylamide. The initiation system polymerized MMA in high yield without side reactions.[6]

In this paper, we describe the polymerization of MMA and *tert*-butyl methacrylate (BMA) using a lithiated PEO diisobutyrate as a new initiator, resulting in linear triblock copolymers having unimodal and narrow molecular weight distributions in high yield.

Experimental Section

Materials. Tetrahydrofuran (THF), toluene, and benzene were distilled twice over $LiAlH_4$ under a nitrogen atmosphere and stored over 4A molecular sieves. Diisopropylamine was distilled over CaH_2 just before use. *n*-Butyllithium was prepared from lithium (metal) and *n*-butyl bromide in hexane and stored under an argon atmosphere. Commercial MMA was purified by the usual method and distilled at reduced pressure.[7] BMA was synthesized from methacrylic acid and isobutene in the presence of concentrated sulfuric acid, purified by vacuum distillation[8] [59.5–59.9 °C (52 mmHg)]. Both monomers were stored under an argon atmosphere.

PEO Diisobutyrate. Five grams of commercial PEO-1000 (M_n = 980) or PEO-4000 (M_n = 2580) was placed into a 50-mL flask equipped with a three-way cock and was freeze-dried from benzene solution. Dry benzene (10 mL) and 1–2 mL of anhydrous pyridine were added in an argon atmosphere. Isobutyryl chloride, 5 times in excess of the PEO hydroxy end groups, was added dropwise to the solution, cooled by a water bath, with vigorous agitation. The reaction mixture was allowed to stand for a day and then transferred to a centrifugal tube and centrifuged to remove the precipitate of pyridine hydrochloride. Supernatant was poured into a large amount of petroleum ether–diethyl ether mixed solvent (2:1 v/v). PEO diisobutyrate (PEDB) was recovered as a white precipitate. Crude PEDB was dried under reduced pressure, purified by repeated centrifugations from benzene solution to remove the pyridine hydrochloride, and reprecipitated into petroleum ether–diethyl ether mixed solvent. From IR, ^1H NMR, and elemental analyses the following results are obtained: IR 1740 cm^{-1} (C=O); ^1H NMR δ 3.63 (s, 87 H for PEDB-1000, 238 H for PEDB-4000, $-(OCH_2CH_2)-_n$), 2.57 (m, 2 H, CH), 1.16 (d, 12 H, CH_3).

Anal. (PEDB-1000) Calcd for $C_{52}H_{102}O_{25}$: C, 55.4; H, 9.06. Found: C, 54.7; H, 9.09. (PEDB-4000) Calcd for $C_{126}H_{250}O_{62}$: C, 54.9; H, 9.08. Found: C, 55.5; H, 9.20.

The molecular weights measured by VPO (M_n = 1100 for

0024-9297/82/2215-0223$01.25/0