Synthesis of Hyperbranched Poly(ester)s with Pendant Hydroxy Groups by the Polyaddition of Bis(oxetane)s with 1,3,5-Benzenetricarboxylic Acid

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ABSTRACT: Hyperbranched poly(ester)s with many pendant primary hydroxy groups were prepared in 21–84% yields by polyadditions of certain bis(oxetane)s such as 1,4-bis[(3-ethyl-3-oxetanylmethoxymethyl)]benzene (BEOB), 1,2-bis[(3-ethy-3-oxetanyl)methoxy]benzene (1,2-BEOMB), 1,3-bis[(3-ethy-3-oxetanyl)methoxy]benzene (1,3-BEOMB), 1,4-bis[(3-ethy-3-oxetanyl)methoxy]benzene (1,4-BEOMB), 4,4′-bis[(3-ethyl-3-oxetanyl)methoxy]biphenyl (4,4′-BEOBP), 3,3′,5,5′-tetramethyl-[4,4′-bis(3-ethyl-3-oxetanyl)methoxy]biphenyl (TM-BEOBP) with 1,3,5-benzenetricarboxylic acid (TMA) using tetraphenylphosphonium chloride (TPPC) as a catalyst in NMP at 140 °C for 12 h. Resulting polymers were insoluble in water; however, these polymers were soluble in 2.3% tetramethylammonium hydroxide aqueous solution. These polymers were also soluble in dioxane, THF, MEK, and aprotic polar solvents. The glass transition temperatures (T_gs) of these polymers were 59–131 °C.   [DOI 10.1295/polymj.38.145]
KEY WORDS   Synthesis of Hyperbranched Poly(ester) / Pendant Hydroxy Group / Polyaddition / Bis(oxetane) / 1,3,5-Benzenetricarboxylic Acid /

Oxetanes as 4-membered cyclic ether have almost the same strain energy[1] (107 kJ/mol) as 3-membered cyclic ether oxiranes. Furthermore, basicities of oxetanes were generally higher than those of oxiranes. Therefore, numerous studies[2] of the cationic polymerization of oxetane compound have been reported. The first commercial polymer of oxetane was PENTONE®, which was prepared by the ring-opening polymerization of 3,3-bis(chloromethyl)oxetane. Very recently, Motoi and his coworkers[3–5] found certain cationic isomerization reactions of oxetane compounds.

However, any other useful ring-opening reactions of oxetane have not been reported excepting our recent research works.[6] Since more than 15 years ago, my research group have studied the development of new ring-opening addition reaction of oxetane and succeeded in finding new reactions of oxetanes such as ring-opening addition reactions with acyl chlorides,[7] phosphonyl chlorides,[8] silyl chloride,[9] active esters,[7] carboxylic acids,[10] phenols,[11,12] and thiols[13] using appropriate quaternary onium salts or crown ether complexes as catalysts. These reactions can be applied practically to the polyadditions of bis(oxetane)s with above reagents such as diacyl chlorides,[14–17] phosphonyl dichlorides,[8] active diesters,[18,19] dicarboxylic acids,[10] bisphenols,[11,12] and dithiols[13] to afford corresponding polymers with high molecular weights. Recently, we also found that an anionic ring-opening polymerization of 2-(hydroxymethyl)oxetanes produced corresponding hyperbranched poly(ether)s containing one terminal oxetanyl groups and many pendant primary hydroxy groups using the complex of potassium *t*-buthoxide with crown ether as a catalyst system,[20–22] and an anionic ring-opening alternating copolymerization[23] of oxetanes with cyclic carboxylic anhydrides using certain quaternary onium salts as catalysts.

The above reaction systems of oxetane compounds and the oxetane polymers prepared by the reactions seem to have great possibility as an important key technology in coatings and electronics fields, and polymer industry in general.

Meanwhile, hyperbranched polymers (HBPs) have recently attracted a great deal of attention as one of the dendritic macromolecules, which have lower viscosity, good solubility and many reactive terminal groups compared with the corresponding linear ones.[24] There are many synthetic methods for the preparation of the HBPs, such as vinyl polymerization[25] and ring-opening polymerization[26] accompanying suitable chain transfer reaction. Furthermore, although HBPs are prepared by the step-wise polymerizations such as polycondensations and polyadditions, in which there are two differential methods; one is the self-condensation[24] (or -addition) reaction of AB$_2$ monomers, however, these monomers are not always commercially available. Another is the polycondensation (or polyaddition) reaction of A$_2$-type monomer with B$_3$-type monomer.[27,28] The latter method is practically advantageous in industrial appli-

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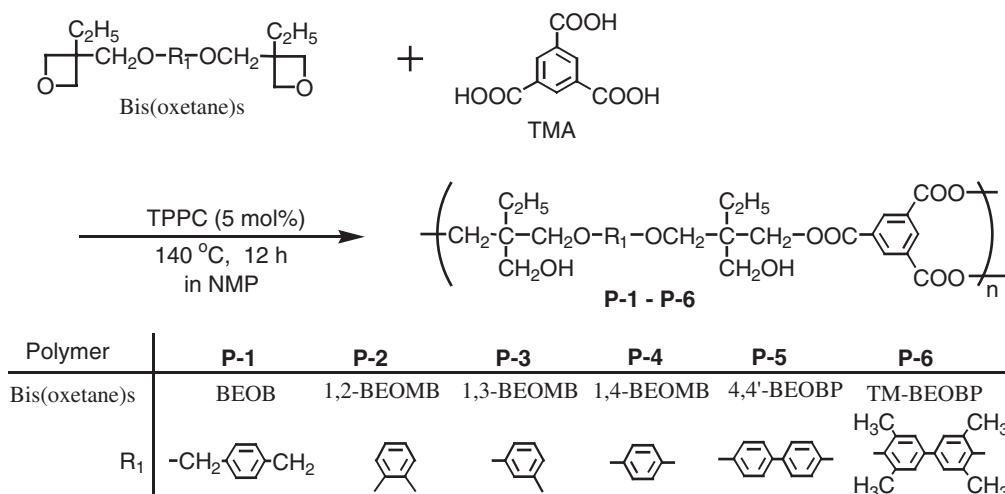
Scheme 1.

cations, because numerous number of monomers are commercially available.

From these backgrounds, in this article, the authors examined the polyaddition of bis(oxetane)s with active 1,3,5-benzenetricarboxylic acid (TMA) for the synthesis of hyperbranched poly(ether)s containing pendant primary hydroxy groups under appropriate reaction conditions (Scheme 1).

EXPERIMENTAL

Materials

The reaction solvents, such as *o*-dichlorobenzene, sulfolane, *N*-methylpyrrolidone (NMP), *N*,*N*-dimethyl-acetamide (DMAc), dimethyl sulfoxide (DMSO), and hexamethylphosphorictriamide (HMPA) were dried with CaH$_2$, and purified by distillation before use. Anisole was dried with Na wire, and purified by distillation before use. Tetrabutylamminoum bromide (TBAB) was recrystalized twice from ethyl acetate. Reagents grade 1,3,5-benzenetricarboxylic acid (TMA), tetrabutylamminoum chloride (TBAC), tetrabutylphosphonium bromide (TBPB), tetrabutylphosphonium chloride (TBPC), tetraphenylphosphonium chloride (TPPC), tetraphenylphosphonium bromide (TPPB), tetraphenylphosphonium iodide (TPPI), 18-crown-6 (18-C-6), potassium chloride (KCl), potassium bromide (KBr), and lithium hydroxide (LiOH) were dried *in vacuo*, and used without further purification. Bis(oxetane)s, 1,4-bis[(3-ethyl-3-oxetanylmethoxymethyl)]benzene (BEOB), 1,2-bis[(3-ethy-3-oxetanyl)methoxy]benzene (1,-BEOMB), 1,3-bis[(3-ethy-3-oxetanyl)methoxy]benzene (1,3-BEOMB), 1,4-bis[(3-ethy-3-oxetanyl)methoxy]benzene (1,4-BEOMB), 4,4′-bis[(3-ethyl-3-oxetanyl)methoxy]biphenyl (4,4′-BEOBP), 3,3′,5,5′-tetramethyl-[4,4′-bis(3-ethyl-3-oxetanyl)methoxy]biphenyl (TM-BEOBP) were donated from Toagosei Co., Ltd.

and were purified by recrystallization from appropriate solvents.

Measurement

Melting points were determined with a Yanako MP-500D hot-stage microscope. Infrared (IR) absorption spectra were measured on a Jasco model FT IR-420 spectrometer. The NMR spectra were recorded on JNM FX-200 (200 MHz for ^{1}H NMR and 50 MHz for ^{13}C NMR) in DMSO-d_6 with Me$_4$Si (TMS) as an internal standard. The number-average molecular weight (M_n) and weight-average molecular weight (M_w) of the polymers were estimated by size exclusion chromatography (SEC; TOSOH model HLC-8020) on TSK gel Multipore Hxl-M columns calibrated by narrow molecular weight polystyrene standards and with tetrahydrofuran (THF) as an eluent without correction using a refractive index detector. Glass transition temperatures (T_g)s were measured on a Seiko Electronic Instruments model EXSTAR 6000/ DSC6200 differential scanning calorimeter (DSC) at a heating rate of 10 °C/min under nitrogen atmosphere. Thermal analysis (TGA) was performed on a Seiko Electronic Instruments model EXSTAR 6000/ TG/DTA 6220 at a heating rate of 10 °C/min under nitrogen.

Synthesis of Hyperbranched Polymer P-1 by Polyaddition of BEOB with TMA

A typical procedure for the polyaddition of BEOB with TMA is as follows: BEOB (0.502 g; 1.5 mmol), TMA (0.210 g; 1.0 mmol), TPPC (0.028 g; 0.075 mmol), and NMP (1.0 mL) were charged to a glass tube in a dry box, after which the tube was evacuated and sealed using a gas torch. The reaction was performed at 140 °C for 12 h in the sealed tube under stirring, and then the tube was opened. The resulting

solution was diluted with a small amount of THF and poured into water (200 mL) containing lithium bromide to precipitate the polymer. The resulting polymer was precipitated twice from THF into excess mixed solvent of *n*-hexane and ether (vol./vol. = 1/1), and dried *in vacuo* at 60 °C for 24 h. The yield of resulting polymer **P-1** was 0.60 g (84%). The number-average moleculer weight (M_n) of the polymer estimated by SEC was 8500 ($M_w/M_n = 2.89$). IR (film): 3438 (ν OH), 1729 (ν C=O, ester), 1461 (ν C=C of aromatic), 1241 (ν C–O–C, ester), 1098 (ν C–O–C, ether), 992 cm^{-1} (ν C–O–C, cyclic ether). ^{1}H NMR (200 MHz, DMSO-d_6, TMS) $\delta = 0.74$–0.85 (m, 7.8H, CH$_2$CH$_3$), 1.37–1.64 (m, 5.7H, CH$_2$CH$_3$), 3.31–3.53 (m, 9.2H, C–CH$_2$–O and CH$_2$–OH), 4.23–4.53 (m, 12.7H, CO$_2$–CH$_2$–C, Ar–CH$_2$–O, C–CH$_2$–O in oxetane ring, and CH$_2$–OH), 7.12–7.34 (m, 5.5H, aromatic H in BEOB unit), 8.51–8.69 ppm (m, 3.0H, aromatic H in TMA unit).

The structure of the hyperbranched polyester was separated into the following three units, a, b, and c (Figure 2) which were calculated from the intensity ratio of proton signal based on 8.51–8.69 ppm protons from TMA unit. Unit ratios of a:b:c = 1:0.24:0.94. The content of the terminal carboxyl groups in the polymer was measured by neutralization titration of the carboxyl groups using KOH aqueous solution in THF (0.01 mol/L). The content of COOH group was 4.81%.

*Synthesis of **P-2** by Polyaddition of 1,2-BEOMB with TMA*

Yield = 21%. $M_n = 2400$, $M_w/M_n = 1.34$. Unit ratios of a:b:c = 1:0.43:0.95. The content of COOH group was 4.31%. IR (film): 3429 (ν OH), 1731 (ν C=O, ester), 1462 (ν C=C, aromatic), 1255 (ν C–O–C ester), 1053 (ν C–O–C, ether), 993 cm^{-1} (ν C–O–C, Cyclic ether). ^{1}H NMR (200 MHz, DMSO-d_6, TMS) $\delta = 0.82$–1.04 (m, 8.1H, CH$_2$CH$_3$), 1.42–1.93 (m, 5.5H, CH$_2$CH$_3$), 3.41–3.78 (m, 4.7H, CH$_2$–OH), 3.78–4.18 (m, 5.5H, C–CH$_2$–O), 4.18–5.15 (m, 8.0H, CO$_2$–CH$_2$–C, C–CH$_2$–O in oxetane ring, and CH$_2$–OH), 6.70–7.08 (m, 5.5H, aromatic H in BEOMB unit), 8.51–8.69 ppm (m, 3.0H, aromatic H in TMA unit).

*Synthesis of **P-3** by Polyaddition of 1,3-BEOMB with TMA*

Yield = 49%. $M_n = 3000$, $M_w/M_n = 1.34$. Unit ratios of a:b:c = 1:0.26:1.01. The content of COOH group was 4.41%. IR (film): 3424 (ν OH), 1730 (ν C=O, ester), 1462 (ν C=C, aromatic), 1241 (ν C–O–C ester), 1056 (ν C–O–C, ether), 992 cm^{-1} (ν C–O–C, Cyclic ether). ^{1}H NMR (200 MHz, DMSO-d_6, TMS) $\delta = 0.82$–1.04 (m, 7.6H, CH$_2$CH$_3$), 1.42–1.93 (m, 5.1H, CH$_2$CH$_3$), 3.41–3.78 (m, 4.3H, CH$_2$–OH),

3.78–4.18 (m, 5.1H, C–CH$_2$–O), 4.18–5.15 (m, 6.7H, CO$_2$–CH$_2$–C, C–CH$_2$–O in oxetane ring, and CH$_2$–OH), 6.24–6.85 (m, 3.8H, aromatic H in BEOMB unit), 6.98–7.25 (m, 1.2H, aromatic H in BEOMB unit), 8.51–8.69 ppm (m, 3.0H, aromatic H in TMA unit).

*Synthesis of **P-4** by Polyaddition of 1,4-BEOMB with TMA*

Yield = 53%. $M_n = 4100$, $M_w/M_n = 1.70$. Unit ratios of a:b:c = 1:0.49:0.88. The content of COOH group was 4.14%. IR (film): 3425 (ν OH), 1730 (ν C=O, ester), 1465 (ν C=C, aromatic), 1240 (ν C–O–C ester), 1052 (ν C–O–C, ether), 993 cm^{-1} (ν C–O–C, Cyclic ether). ^{1}H NMR (200 MHz, DMSO-d_6, TMS) $\delta = 0.82$–1.04 (m, 7.4H, CH$_2$CH$_3$), 1.42–1.93 (m, 5.5H, CH$_2$CH$_3$), 3.41–3.78 (m, 5.1H, CH$_2$–OH), 3.78–4.18 (m, 5.1H, C–CH$_2$–O), 4.18–5.15 (m, 7.4H, CO$_2$–CH$_2$–C, C–CH$_2$–O in oxetane ring, and CH$_2$–OH), 6.70–7.08 (m, 5.5H, aromatic H in BEOMB unit), 8.51–8.69 ppm (m, 3.0H, aromatic H in TMA unit).

*Synthesis of **P-5** by Polyaddition of 4,4'-BEOBP with TMA*

Yield = 74%. $M_n = 6200$, $M_w/M_n = 1.74$. Unit ratios of a:b:c = 1:0.62:0.97. The content of COOH group was 3.77%. IR (film): 3430 (ν OH), 1731 (ν C=O, ester), 1470 (ν C=C, aromatic), 1255 (ν C–O–C ester), 1053 (ν C–O–C, ether), 993 cm^{-1} (ν C–O–C, Cyclic ether). ^{1}H NMR (200 MHz, DMSO-d_6, TMS) $\delta = 0.85$–1.04 (m, 8.5H, CH$_2$CH$_3$), 1.42–1.98 (m, 56.4H, CH$_2$CH$_3$), 3.43–3.78 (m, 5.12H, CH$_2$–OH), 3.78–4.18 (m, 5.7H, C–CH$_2$–O), 4.18–5.35 (m, 8.0H, CO$_2$–CH$_2$–C, C–CH$_2$–O in oxetane ring, and CH$_2$–OH), 6.65–7.12 (m, 5.4H, aromatic H in BEOBP unit), 7.12–7.64 (m, 5.4H, aromatic H in BEOBP unit), 8.51–8.69 ppm (m, 3.0H, aromatic H in TMA unit).

*Synthesis of **P-6** by Polyaddition of TM-BEOBP with TMA*

Yield = 79%. $M_n = 6900$, $M_w/M_n = 2.14$. Unit ratios of a:b:c = 1:0.42:1.03. The content of COOH group was 4.16%. IR (film): 3430 (ν OH), 1731 (ν C=O, ester), 1474 (ν C=C, aromatic), 1238 (ν C–O–C ester), 1066 (ν C–O–C, ether), 988 cm^{-1} (ν C–O–C, cyclic ether). ^{1}H NMR (200 MHz, DMSO-d_6, TMS) $\delta = 0.82$–1.04 (m, 8.6H, CH$_2$CH$_3$), 1.40–1.95 (m, 6.2H, CH$_2$CH$_3$), 1.95–2.38 (m, 16.2H, Ar–CH$_3$), 3.43–3.90 (m, 9.4H, CH$_2$–OH, C–CH$_2$–O), 4.02–5.02 (m, 8.6H, CO$_2$–CH$_2$–C, Ar–CH$_2$–O, C–CH$_2$–O in oxetane ring, and CH$_2$–OH), 6.65–7.35 (m, 6.2H, aromatic H in TM-BEOBP unit), 8.40–8.98 ppm (m, 3.0H, aromatic H in TMA unit).

RESULTS AND DISCUSSION

Since the polyaddition of bis(oxetane)s with dicarboxylic acids proceeded at 140 °C to produce corresponding polyesters with high molecular weight, the catalytic effect of the polyaddition of BEOMB with TMA was examined at 140 °C for 12 h.

When the reaction was performed without any catalyst, oligomer with low molecular weight ($M_n = 2200$) was obtained in only 13% yield. However, the yields and M_n increased using following catalysts. As summarized in Table I, tetraphenyl onium salts such as TPPC, TPPB, and TPPI showed higher catalytic activity than other tetrabutyl onium salts such as TBAC, TBAB, TBPB, and TBPB from the view points of molecular weight and yield of the polymer. This may be due to the higher thermal stability[29,30] of tetraphenyl onium salts than that of tetrabutyl onium salts. However, the activities of complexes of 18-crown-6 with KCl and KBr were lower than those of tetraphenyl onium salts. This may be due to the less solubility of the crown ether complexes into the reaction medium.

This means that quaternary onium salts or crown ether complexes, especially tetraphenyl onium salts are appropriate as catalyst for the polyaddition of bis(oxetane) with TMA to form hyperbranched polymer.

The structure of the obtained polymer **P-1** was confirmed by the IR and ^{1}H NMR spectroscopy. In the IR spectrum of the polymer film, the absorption peak at 992 cm^{-1} assignable to the cyclic C–O–C stretching from oxetane ring decreased, and showed a new appearance of characteristic absorption peaks at 3438 cm^{-1} assignable to the pendant OH group, and at 1729, and 1241 cm^{-1} assignable to the C=O and C–O–C (ester) stretching from alkyl ester linkage, respectively. The ^{1}H NMR spectrum of this polymer showed signals at $\delta = 0.74$–0.85 due to –CH$_2$–C$\underline{H}_3$, 1.37–1.64 due to –C$\underline{H}_2$CH$_3$, 3.31–3.53 due to O–C$\underline{H}_2$–C and C$\underline{H}_2$–OH, 4.23–4.53 due to CO$_2$–C$\underline{H}_2$–C, Ar–C$\underline{H}_2$–O, C–C$\underline{H}_2$–O in oxetane ring, and CH$_2$–O$\underline{H}$, 7.12–7.34 due to aromatic protons in BEOB unit, and 8.51–8.69 ppm due to aromatic protons in TMA unit (Figure 1). Furthermore, many terminal carboxyl groups were confirmed by neutralization titration. From these analytical data, although the degree of

Table I. The polyaddition of BEOB with TMA using certain catalysts[a]

Run	Catalyst	Yield (%)[b]	$M_n \times 10^{-3}$ [c]	M_w/M_n [c]
1	None	13	2.2	1.35
2	TBAC	55	4.6	1.74
3	TBAB	53	4.0	1.88
4	TBPC	72	5.8	2.11
5	TBPB	71	5.7	2.11
6	TPPC	84	8.5	2.89
7	TPPB	80	7.2	2.99
8	TPPI	82	7.5	4.90
9	18-C-6/KCl	52	4.0	1.76
10	18-C-6/KBr	39	3.1	1.72

[a]The reaction was carried out with BEOB (1.5 mmol) and TMA (1.0 mmol) using 5 mol% of various catalysts in NMP (1.0 mL) at 140 °C for 12 h. [b]Insoluble parts in water and *n*-hexane and diethyl ether. [c]Estimated by GPC (DMF) based on polystyrene standards.
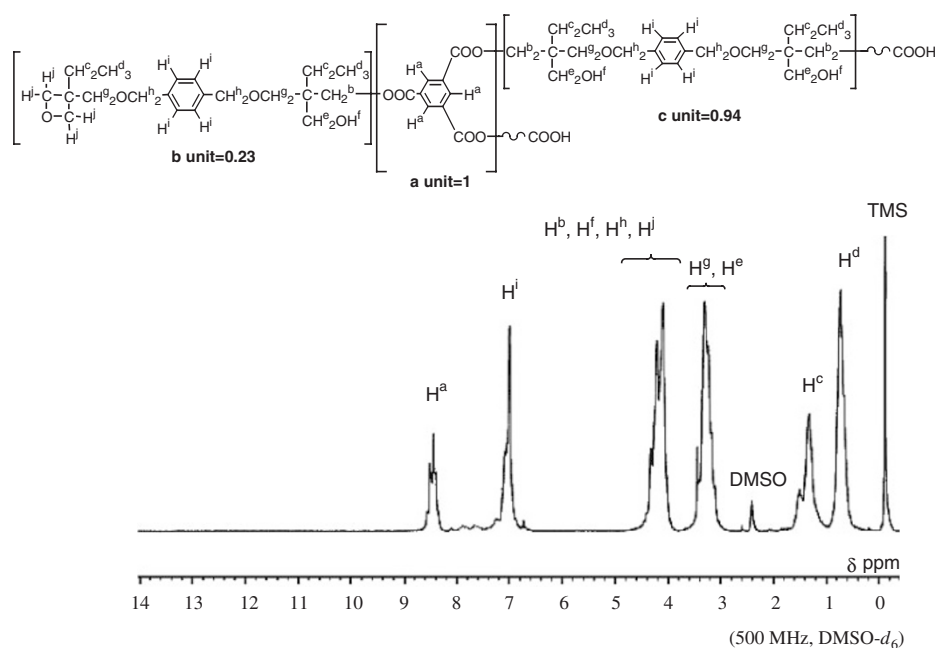

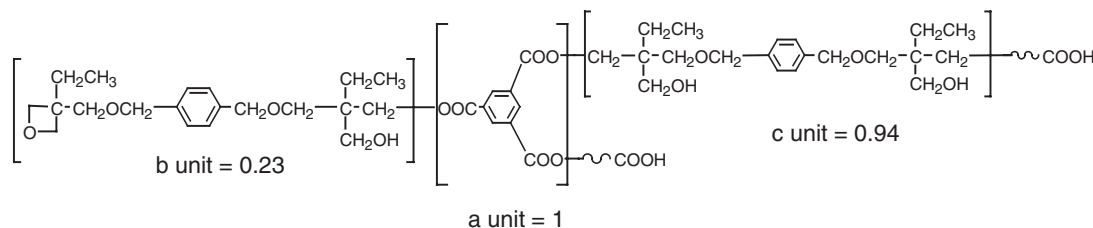**Figure 1.** ^{1}H NMR spectrum of hyperbranched polymer **P-1**.

Figure 2. The structure of hyperbranched polymer **P-1**.

Table II. The polyaddition of BEOB with TMA
in certain solvents[a]

Run	Solvent	Yield (%)[b]	$M_n \times 10^{-3}$ [c]	M_w/M_n [c]
1	None	—	—	—
2	Anisole	—	—	—
3	o-Dichlorobenzene	—	—	—
4	DMSO	37	4.2	1.86
5	DMAc	80	5.7	2.49
6	NMP	84	8.5	2.89
7	HMPA	83	9.3	5.28
8	Sulfolane	81 (15)	14.2	20.39

[a]The reaction was carried out with BEOB (1.5 mmol) using
5 mol % of TPPC in various solvent at 140 °C for 12 h.
[b]Insoluble parts in water and n-hexane and diethyl ether.
[c]Estimated by GPC (DMF) based on polystyrene standards.
[d]Insoluble parts in THF.

Figure 3. Effect of reaction temperature on the polyaddition
of BEOB with TMA. The reaction was carried out with BEOB
(1.5 mmol) with TMA (1.0 mmol) using TPPC (5 mol %) as the
catalyst in NMP (1.0 mL) for 12 h. (●): M_n, (■): Yield.

branching of the resulting polymer could not be calcu-
lated, we can suggest the following repeating units
such as **a** = 0.23 and **c** = 0.94 of the polymer struc-
ture based on the value **b** = 1.0 (Figure 2).

We examined the effect of reaction medium under
the same conditions using TPPC as the catalyst, which
has the highest activity. As summarized in Table II,
the polyaddition of BEOB with TMA proceeded in
DMSO, DMAc, NMP, and HMPA to give the soluble
polymers (Table II). This suggests that the yields and
M_n of the resulting polymers increased with dipole
moment of the used aprotic polar solvents excepting
DMSO.[31] However, 81 wt % of soluble polymer and
15 wt % of insoluble gel products were obtained from
the reaction in sulfolane, which had very high dipole
moment among them. On the other hand, no reaction
occurred in anisole and o-dichlorobenzene, and in
bulk, because TMA was insoluble in these solvent
and BEOB under this reaction condition.

This means that NMP is a suitable reaction solvent
for the polyaddition of BEOB with TMA to afford
corresponding hyperbranched polyester containing
many pendant hydroxy groups.

We also examined the effect of reaction tempera-
ture and the time using TPPC in NMP. As shown in
Figure 3, although no reaction occurred at 100 °C
for 12 h, the yields and M_ns of soluble hyperbranched
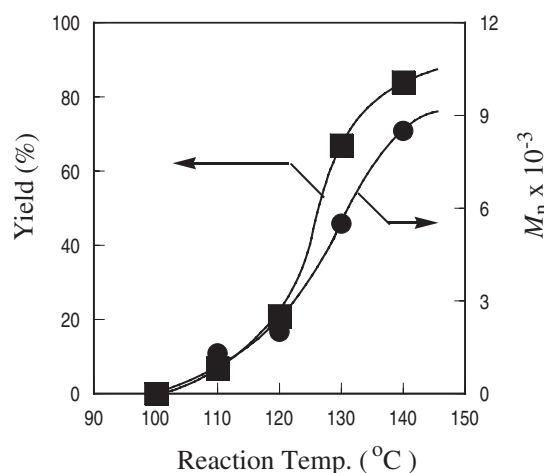polymers increased gradually with temperatures at

110–140 °C for 12 h. However, when the polyaddition
was performed at 150 °C for 12 h, 84 wt % of insoluble
gel products and 14 wt % of soluble products were ob-
tained. In addition, the molecular weight distribution
(M_w/M_n) of the obtained soluble products in this reac-
tion was 26.06. Therefore, it seems that 140 °C was
suitable reaction temperature to obtain soluble hyper-
branched polymer in good yields under this reaction
condition.

As shown in Figure 4, the yields and M_n of the
soluble polymers increased with reaction time at 3–
15 h when the polyaddition of BEOB with TMA
was carried out at 140 °C in NMP using TPPC as a
catalyst. However, 63 wt % of insoluble gel products
and 31 wt % of soluble products were obtained when
the reaction was performed for 18 h. It was also found
that the molecular weight distribution of the obtained
soluble polymers broadened with reaction time. This
shows that reaction temperature and time are impor-
tant factor to obtain soluble hyperbranched polymers
in good yields.

The effect of feed ratio of TMA was examined at
140 °C for 12 h in NMP using 5 mol % of TPPC as
the catalyst. As summarized in Table III, hyper-
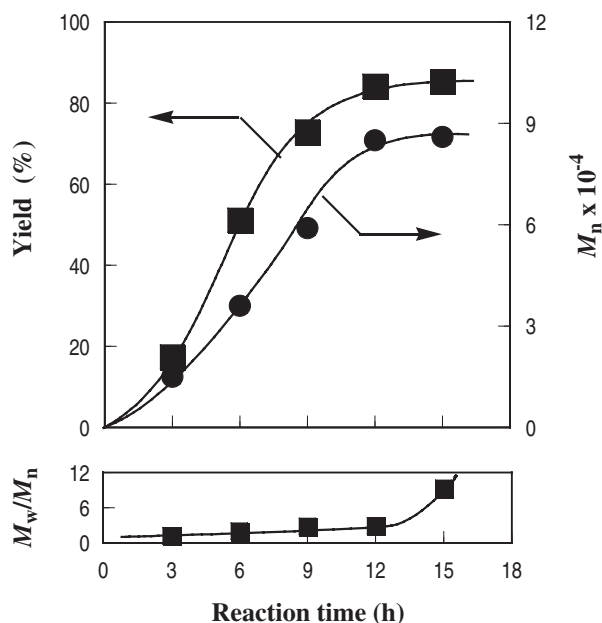branched polymer with the highest molecular weight

Figure 4. Effect of reaction time on the polyaddition of BEOB with TMA. The reaction was carried out with BEOB (1.5 mmol) with TMA (1.0 mmol) using TPPC (5 mol %) as the catalyst in NMP (1.0 mL) at 140 °C. ($\bullet$): M_n, ($\blacksquare$): Yield.

was obtained, when the reaction was performed with equivalent molar ratio of BEOB with TMA, and it was found that the molecular weights decreased with increasing or decreasing TMA. It is also suggested that **b** unit contents increased with increasing feed ratio of BEOB, and carboxyl group contents increased with increasing feed ratio of TMA under this reaction condition.

From the above information, polyadditions of other bis(oxetane)s such as 1,2-BEOMB, 1,3-BEOMB, 1,4-BEOMB, 4,4′-BEOBP, and TM-BEOBP with TMS were examined using 5 mol % of TPPC as a catalyst in DMAc at 140 °C for 24 h, and all the results are summarized in Table IV. Polyadditions of 4,4′-BEOBP and TM-BEOBP with TMA produced corresponding hyperbranched polymers (**P-5**, **P-6**) with relatively high molecular weights in satisfactory yields, respectively. However, the yields and molecular weights of **P-2**, **P-3**, and **P-4** were not high enough by the polyadditions of BEOMBs with TMA, respectively.

Glass transition temperatures (T_g)s and weight loss temperatures (T_d)s of the synthesized polymers **P-1**–

Table III. Effect of feed ratio of TMA on the polyaddition with BEOB[a]

Run	TMA (mmol)	Yield (%)[b]	$M_n \times 10^{-3}$ [c]	M_w/M_n [c]	Unit ratio[d] a:b:c	COOH (%)
1	0.5	48	4.9	1.63	1:0.71:1.18	1.52
2	0.7	49	5.2	2.02	1:0.42:0.98	2.17
3	0.9	73	6.7	1.97	1:0.38:0.98	4.01
4	1.0	84	8.5	2.89	1:0.23:0.95	4.81
5	1.1	81	8.0	2.29	1:0.20:0.98	5.38
6	1.3	62	7.0	3.04	1:0.19:0.94	6.18
7	1.5	52	5.9	2.99	1:0.06:0.60	7.54

[a]The reaction was carried out with BEOB (1.5 mmol) and TMA using 5 mol % of TPPC in various solvent at 140 °C for 12 h. [b]Insoluble parts in water and *n*-hexane and diethyl ether. [c]Estimated by GPC (DMF) based on polystyrene standards. [d]Estimated by ^{1}H NMR. [e]Estimated by titration of carboxyl groups in polymer.

Table IV. The polyaddition of certain bis(oxetane)s with TMA[a]

Run	Polymer	Yield (%)[b]	$M_n \times 10^{-3}$ [c]	M_w/M_n [c]	COOH (%)[d]	T_g (°C)[e]	$T_d^{5\%}$ [f]
1	**P-1**	84	8.5	2.89	4.81	59	331
2	**P-2**	21	2.4	1.34	4.31	77	328
3	**P-3**	49	3.0	1.37	4.41	78	321
4	**P-4**	53	4.1	1.70	4.14	84	335
5	**P-5**	74	6.2	1.74	3.77	131	376
6	**P-6**	79	6.9	2.14	4.16	120	348

[a]The reaction was carried out with Bis(oxetane) (1.5 mmol) and TMA (1 mmol) using 5 mol % of TPPC in NMP 1.5 mL at 140 °C for 12 h. [b]Insoluble parts in water and *n*-hexane and diethyl ether. [c]Estimated by GPC (DMF) based on polystyrene standards. [d]Estimated by titration of carboxy group in polymer. [e]Determined by DSC at heating rate 10 °C/min in nitrogen. [f]Determined by TG/DTA at heating rate 10 °C/min in nitrogen.

Table V. Solubility of hyperbranched polyesters **P-1**–**P-6**

Solvent	Polyester					
	P-1	**P-2**	**P-3**	**P-4**	**P-5**	**P-6**
Water	−	−	−	−	−	−
Hexane	−	−	−	−	−	−
Cyclohexane	−	−	−	−	−	−
Toluene	−	−	−	−	−	−
1,4-Dioxane	++	++	++	++	++	++
Diethyl ether	−	−	−	−	−	−
Chloroform	++	++	++	++	++	++
Anisole	−	+	+	+	−	−
Chlorobenzene	−	−	−	−	−	−
Methanol	++	++	++	++	−	−
Ethanol	++	++	++	++	−	−
THF	++	++	++	++	++	++
Ethyl acetate	−	−	−	−	−	−
o-Dichlorobenzene	−	−	−	−	−	−
Acetone	++	++	++	++	++	++
Acetonitrile	−	−	−	−	−	−
MEK	++	++	++	++	++	++
DMAc	++	++	++	++	++	++
DMF	++	++	++	++	++	++
NMP	++	++	++	++	++	++
DMSO	++	++	++	++	++	++
HMPA	++	++	++	++	++	++
1 wt % Na$_2$CO$_3$ aq.	+−	+−	+−	+−	+−	+−
2.38 wt % TMAH	++	++	++	++	++	++

[a]++; soluble at room temperature. +; soluble by heating. +−; partially soluble or swelling. −; insoluble.

P-6 were measured by DSC and TGA, respectively. As summarized in Table IV, **P-5** and **P-6** composed from BEOBP unit showed high T_gs such as 131 and 120 °C, respectively. On the other hand the T_g of **P-1** prepared from relatively flexible unit BEOB was 59 °C. Polymers **P-2**, **P-3**, and **P-4** prepared from BEOMB unit showed T_gs at 77, 78, and 84 °C, respectively. This result shows that the T_gs of the obtained hyperbranched polyesters were strongly affected by the structure of the repeating units.

Furthermore, we examined 5 wt % loss temperatures ($T_d{}^{5\%}$) of all the obtained hyperbranched polymers. As summarized in Table IV, $T_d{}^{5\%}$ of **P-5** and **P-6** were 376 and 348 °C, respectively, which are higher than those of **P-1**, **P-2**, **P-3**, and **P-4**. On the other hand, $T_d{}^{5\%}$ of **P-1**, **P-2**, **P-3**, and **P-4** were 331, 328, 321, and 335 °C, respectively. This result suggests that the thermal decomposition temperatures of the hyperbranched polyesters were also strongly influenced by the molecular structure of the repeating units. Consequently, both T_g and thermal stability of the hyperbranched polymers containing biphenyl moieties as repeating units were higher than those of other hyperbranched polymers.

All the obtained hyperbranched polyesters **P-1**–**P-6** containing many pendant primary hydroxy groups were insoluble in water. However, interestingly enough, it was found that these polymers were well soluble in 2.38% TMAH aqueous solution, and partly soluble or swelling in 1% sodium carbonate aqueous solution. These polymers also showed characteristic solubility to organic solvents. That is, although these polymers were ordinarily insoluble in aromatic solvents, n-hexane, cyclohexane, diethyl ether, and acetonitrile, and were soluble in chloroform, THF, MEK, and aprotic polar solvents such as DMF, DMAc, NMP, DMSO, and HMPA. Furthermore, polymers **P-1**–**P-4** were soluble in methanol and ethanol. However, polymers **P-5** and **P-6** were insoluble in the alcohols. That is, the solubility of the obtained hyperbranched polyesters was strongly influenced by the polymer structure.

CONCLUSIONS

We demonstrated the synthesis of the novel hyperbranched poly(ester)s containing many pendant primary hydroxy groups by the polyaddition of bis(oxetane)s and TMA. The reaction of bis(oxetane)s with TMA proceeded smoothly using tetraphenylphosphonium halides as catalysts at 140 °C for 12 h in NMP, affording the corresponding hyperbranched poly(ester)s. The certain characteristic properties such as thermal properties and solubility of the synthesized hyperbranched polymers were evaluated, and it was found that these properties were strongly influenced by their structures. Furthermore, it is expected that the synthesized hyperbranched polymers are useful functional materials.

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