ORIGINAL ARTICLE

Azidation of polyesters having pendent functionalities by using NaN_3 or DPPA–DBU and photo-crosslinking of the azidopolyesters

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In this article, we performed dehydration polycondensation of bromosuccinic acid and methylsuccinic acid with 1,4-butanediol at 80 °C to synthesize aliphatic polyesters containing pendent bromo groups without dehydrobromination using scandium trifluoromethanesulfonate ($\text{Sc}(\text{OTf})_3$) as the catalyst. Azidation of the resultant polyesters was carried out readily in *N,N*-dimethylformamide at room temperature using sodium azide ($M_n=8.3 \times 10^3$ ($M_w/M_n=2.17$)). ^1H nuclear magnetic resonance analysis of the product revealed that 65% contained azide functionality, and dehydrobromination occurred in 35% during the azidation process. On the other hand, azidation of poly(butylene bromoadipate-*co*-butylene methylsuccinate) (poly(BBA-*co*-BMS)) proceeded successfully under the same conditions to generate poly(butylene azidoadipate-*co*-butylene methylsuccinate) (poly(BAA-*co*-BMS)) without dehydrobromination ($M_n=10.4 \times 10^3$ ($M_w/M_n=2.71$)). We successfully photo-crosslinked the resultant azidopolyester by ultraviolet irradiation and examined it using scanning electron microscope. We also described azidation of polyesters having pendent hydroxyl groups by using the 'DPPA (diphenylphosphoryl azide)–DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) substitution strategy' to produce water-soluble polyesters containing pendent azido groups ($M_n=7.5 \times 10^3$ ($M_w/M_n=2.25$)). These azidopolyesters might be extremely useful not only for their derivatization by simple chemical modification but also for their effective utilization as photolithography material.

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INTRODUCTION

Aliphatic polyesters have been the subject of intensive research owing to their wide applications in chemistry and biology, and in technologies. Some of the most common examples include poly(L-lactic acid), poly(glycolic acid), poly(ϵ -caprolactone) and their copolymers.¹ Despite their utilities, there remains a need to design materials with more variation in solubility, crystallinity, polarity and reactivity.

There are few publications reporting the chemical synthesis of linear polyesters having pendent azido groups. For example, Jerome *et al.*^{2,3} reported a ring-opening polymerization strategy for synthesizing polyesters. First, statistical copolymerization of α -chloro- ϵ -caprolactone with ϵ -caprolactone was initiated by 2,2-dibutyl-2-stannal-1,3-dioxepane. In the second step, pendent chlorides were converted into azides by reaction with sodium azide. However, the scope of the polymer architecture achieved by this method is generally limited by the availability of structurally diverse monomers. On the other hand, a strategy involving polycondensation of dicarboxylic acid and diol could apply equally to various monomers.

Recently, we reported direct polycondensation of dicarboxylic acids with diols at room temperature, a reaction that was catalyzed using rare-earth trifluoromethanesulfonate to yield aliphatic polyesters with M_n of $>1.0 \times 10^4$ (refs 4, 5). Under mild conditions, it was possible to use this polycondensation method for thermally unstable monomers containing a carbon–carbon double bond⁶ as well as bromine substituent,⁶ and/or hydroxyl^{7,8} functionalities (chemoselective dehydration polycondensation).^{7,8}

In this paper, we describe the synthesis of polyesters having pendent azido groups. Generally, monomeric organic azide is explosive. Therefore, to eliminate as much as possible, any procedure involving these dangerous monomeric organic azides, we performed azidation of polyester having pendent functionalities. First, the synthesis proceeded under mild conditions by chemoselective dehydration polycondensation between diols and dicarboxylic acids having pendent bromo or hydroxyl groups, including bromosuccinic acid (BSA), bromoadipic acid and L-tartaric acid (L-TA). Second, azidation of polyesters having pendent bromo and hydroxyl groups were carried out in

N,N-dimethylformamide (DMF) at room temperature using either sodium azide (Scheme 1) or the 'DPPA-DBU method'⁹ (Scheme 2). On ultraviolet (UV) irradiation, azides generate highly unstable nitrene radicals that react with the surrounding polymer backbone, yielding covalent crosslinks.¹⁰ The nitrene are so reactive that they attack various chemical bonds including the C–H, N–H and O–H bonds, reduction of which leads to the corresponding amines. In the case of aryl azides, a number of ring expansion reactions have also been observed.¹¹

Here, we have successfully demonstrated the UV light-induced photo-crosslinking of the azidopolyesters without the use of any photo- or radical-initiator (refs 12 and 13, respectively, which describe the synthesis and photo- or radical-induced crosslinking of aromatic and aliphatic polyesters having double bond). To the best of our knowledge, although there are many reports of photo-crosslinking of the vinyl polymer having pendent azido groups,^{14,15} at present there are no known published reports on the application of polyesters having pendent azido groups in lithography. This polycondensation system makes it possible to use various monomers and control a solubility, biodegradability, physical and hydrolysis properties⁸ as photo-crosslinked materials.

EXPERIMENTAL PROCEDURE

Materials

BSA and methylsuccinic acid (MSA) were obtained from Sigma-Aldrich Co. (St Louis, MO, USA). L-TA, fumaric acid (FA) and diethylene glycol (DEG) were purchased from Nacalai Tesque (Kyoto, Japan). 1,4-Butanediol (1,4-BD) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) were obtained from Tokyo Kasei Co. (Tokyo, Japan). Scandium trifluoromethanesulfonate (Sc(OTf)₃), sodium

azide (NaN₃) and bis(*p*-nitrophenyl) azidophosphonate (*p*-NO₂DPPA)¹⁶ were purchased from Wako Pure Chemical (Osaka, Japan). 2-Bromoadipic acid (BAA)¹⁷ was prepared in our laboratory. DMF, tetrahydrofuran, chloroform, diethyl ether, acetone and H₂O were purified by distillation before use.

Low-temperature polycondensation of diols with dicarboxylic acids having pendent functionalities

In this work, a typical polycondensation procedure was carried out as follows. For poly(butylene bromosuccinate) (poly(BBS)): in a 10 ml round bottom flask, BSA (1.0 mmol), 1,4-BD (1.0 mmol) and Sc(OTf)₃ (0.01 mmol) were mixed and stirred at 80 °C for 1 h. The polycondensation started under 30 mm Hg. After 6 h, the pressure was gradually reduced to 0.3–3 mm Hg and the reduced pressure was maintained for 30 h to complete the condensation. After re-precipitating the product from the reaction mixture using CHCl₃ and diethyl ether, the yield of the product was 88%. ¹H nuclear magnetic resonance (NMR; 200 MHz, CDCl₃, δ, p.p.m.): 1.71–1.80 (4H, OCH₂CH₂), 2.93–3.05 and 3.22–3.35 (2H, CHBrCH₂), 3.72 (t, 6.5 Hz, –CH₂OH (terminus)), 4.16 (2H, CH₂COOCH₂), 4.23 (2H, CHBrCOOCH₂) and 4.53–4.61 (1H, COCHBr). ¹³C NMR (50 MHz, CDCl₃, δ, p.p.m.): 25.0 (OCH₂CH₂), 38.0 (CH₂CHBr), 39.6 (CH₂CHBr), 64.5 and 65.5 (OCH₂CH₂), 169.0 and 169.6 (COOCH₂). FT IR (KBr disk, cm^{–1}): 2960 (ν_{C–H}), 1737 (ν_{C=O} (ester)), 1467 and 1395 (δ_{C–H}), 1334 (δ_{C–Br}), 1260 and 1164 (ν_{C–O} (ester)). For poly(diethylene glycolyl L-tartrate) (poly(L-TA-co-DEG)): in a 10 ml round bottom flask, L-TA (2.0 mmol), DEG (2.0 mmol) and Sc(OTf)₃ (0.02 mmol) were mixed and stirred at 80 °C under 30 mm Hg for 1 h. After 2 h, the pressure was gradually reduced to 0.3–3 mm Hg and the reduced pressure was maintained for 10 h to complete the condensation. After precipitating the product from the reaction mixture using H₂O and acetone, the yield of the final product turned out to be 64%. ¹H NMR (200 MHz, DMSO-*d*₆, δ, p.p.m.): 3.51–3.75 (4H, COOCH₂CH₂), 4.04–4.49 (6H, COOCH₂, OHCH) and 5.46–5.60 (2H, CHOCH). ¹³C NMR (50 MHz, DMSO-*d*₆, δ, p.p.m.): 60.2 (–CH₂OH

Scheme 1 Azidation of polyesters having pendent bromo functionalities by NaN₃. 1,4-BD, 1,4-butanediol; BAA, 2-bromoadipic acid; BSA, bromosuccinic acid;). DMF, *N,N*-dimethylformamide; MSA, methylsuccinic acid.

Scheme 2 Azidation of polyesters having pendent hydroxyl functionalities by using the DPPA (diphenylphosphoryl azide)-DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) method. DEG, diethylene glycol; DMF, *N,N*-dimethylformamide; L-TA, L-tartaric acid.

(terminus)), 63.9 (COOCH₂), 68.2 (COOCH₂CH₂), 72.4 (CHOH) and 171.2 (COO). FT IR (KBr disk, cm⁻¹): 3426 (ν_{O-H}), 2924 (ν_{C-H}), 1744 (ν_{C=O} (ester)), 1400 (δ_{C-H}), 1277 and 1213 (ν_{C-O} (ester)), 1131 (ν_{C-O} (ether)) and 1092 (ν_{C-O}).

Azidation of polyesters containing pendent bromo groups using NaN₃

A typical azidation procedure using NaN₃ is as follows: in a flask, 103 mg (0.37 mmol) of poly(butylene bromoadipate) (poly(BBA)) was dissolved in 1.9 ml DMF. Under low-light condition, 24 mg (0.37 mmol) of NaN₃ was added to the solution and the reaction was carried out at room temperature for 1 h, following which the solvent was evaporated off. The remaining crude contents of the flask were extracted with excess CHCl₃ to solubilize the product and the solution was further filtered to eliminate impurities. The filtrate was then evaporated off to obtain the dry product (66% yield). ¹H NMR (200 MHz, CDCl₃, δ, p.p.m.): 1.49–2.00 (8H, COCHN₃CH₂CH₂CH₂COO, OCH₂CH₂CH₂CH₂O, COCHN₃CH₂), 2.25–2.47 (2H, COCHN₃CH₂CH₂CH₂), 3.66–3.71 (–CH₂OH (terminus)), 3.82–3.91 (1H, COCHN₃), 4.07–4.15 (2H, COOCH₂) and 4.18–4.28 (2H, COOCH₂CH₂CH₂CH₂).

Preparation of azidopolyester film

The azidopolyester (run 5 in Table 1) was dissolved in CHCl₃ (5 wt%) and the resulting solution was then used for spin-coating a silicon wafer at 3000 r.p.m. The coating was performed using an MIKASA SPINCOATER 1H-D7 (MIKASA, Tokyo, Japan). The resulting azidopolyester film was prebaked at 65 °C for 2 min and then at 95 °C for 5 min in an oven.

UV-irradiation and development of the azidopolyester film

The film was irradiated with a high-pressure mercury lamp (H-400P, Toshiba, Tokyo, Japan) for 15 min through a negative photomask using a contact technique. Thereafter, the exposed film was post-baked at 125 °C for 5 min in an oven, and developed by dipping in CHCl₃ at room temperature.

Azidation of polyesters containing pendent hydroxyl functionality by the DPPA (diphenylphosphoryl azide)–DBU (1,8-diaza-bicyclo[5.4.0]undec-7-ene) method

A typical azidation procedure using the DPPA–DBU method is described briefly as follows. In a flask, poly(L-TA-co-DEG) (1.8 mmol of hydroxyl content) was dissolved in 1.8 ml of DMF. Under dimmed light condition, DBU (2.7 mmol) and *p*-NO₂DPPA (2.7 mmol) were added into the solution. The mixture was continuously stirred at room temperature for 12 h. After the reaction was completed, the solution was poured in excess acetone. The precipitate was then dialyzed against water by cellulose ester (CE) dialysis membranes (MWCO 1000 cutoff; Spectrum Laboratories Inc., Rancho Dominguez, CA, USA) for 2 days to remove byproducts (59% yield, run 3 in Table 2). The purified product was analyzed by NMR and IR spectroscopy and the results are summarized below. ¹H NMR (200 MHz, DMSO-*d*₆, δ, p.p.m.): 3.61–3.78 (2H, COOCH₂CH₂), 4.01–4.37 (3H, COOCH₂, COCHN₃), 4.41–4.49 (1H, COCHOH), 4.66–4.90 (1H, COCHN₃CHOH) and 5.14–5.37 (2H, COCHOHCHOH). ¹³C NMR (50 MHz, DMSO-*d*₆, δ, p.p.m.): 64.0 (COOCH₂), 68.2 (COCHN₃), 68.3 (COOCH₂CH₂), 72.4 (COCHOHCHOH), 74.9 (COCHN₃CHOH) and 171.4 (COO). FT IR (KBr disk, cm⁻¹): 3426 (ν_{O-H}), 2924 (ν_{C-H}), 2125 (ν_{N₃} (azide)), 1744 (ν_{C=O} (ester)), 1400 (δ_{C-H}), 1277 and 1213 (ν_{C-O} (ester)), 1131 (ν_{C-O} (ether)) and 1092 (ν_{C-O}).

Table 1 Azidation of poly(butylene bromosuccinate) or poly(butylene bromosuccinate-co-butylene methylsuccinate) by NaN₃^a

Run	BSA/MSA/1,4-BD Feed ratio	Temp. (°C)	Yield (%)	$M_n^b \times 10^{-3} (M_w/M_n^b)$		Residual azide ratio ^c (%)	Double bond ^d (%)	Crosslinking ^e (%)
				Before azidation	After azidation			
1	50:00:50	27	73	—	—	69	31	—
2	17:33:50	27	58	—	—	68	32	—
3	17:33:50	40	70	—	—	74	18	8
4	17:33:50	60	64	—	—	78	7	15
5	10:40:50	27	74	7.6 (1.71)	8.3 (2.17)	65	35	—
6	10:40:50	27	70	—	—	68	32	—
7	10:40:50	40	90	—	—	71	19	10
8	10:40:50	60	90	—	—	63	1	36

Abbreviations: 1,4-BD, 1,4-butanediol; BSA, bromosuccinic acid; MSA, methylsuccinic acid.

^aAll azidation runs were performed for 1 h (except for run 5: azidation was performed for 5 h) in *N,N*-dimethylformamide (DMF), [polyester]₀=0.2 M (except for run 5: [polyester]₀=0.08 M) in DMF, [bromo group]₀/[NaN₃]₀=1.0.

^bDetermined by size exclusion chromatography in CHCl₃ relative to poly(styrene)s.

^cDetermined by ¹H nuclear magnetic resonance spectrum.

Table 2 Azidation of poly(butylene bromoadipate) or poly(butylene bromoadipate-co-butylene methylsuccinate) by NaN₃^a

Run	BAA/MSA/1,4-BD ratio		Yield (%)	$M_n^b \times 10^{-3} (M_w/M_n^b)$		Azidation ratio ^c (%)	T _g ^d (°C)	T _m ^e (°C)	ΔH ^f (°C)
	Feed	Observed ^d		Before azidation	After azidation				
1	50:00:50	50:00:50	66	5.6 (2.29)	5.3 (2.23)	>99	–54	—	—
2	17:33:50	17:33:50	49	11.0 (2.46)	10.4 (2.71)	>99	–43	52	6.7
3	10:40:50	9:41:50	58	10.4 (2.25)	9.7 (2.42)	>99	–45	45	6.6

Abbreviations: 1,4-BD, 1,4-butanediol; BSA, bromosuccinic acid; MSA, methylsuccinic acid.

^aAll azidation runs were performed at 27 °C for 1 h in *N,N*-dimethylformamide, [polyester]₀=0.2 M, [bromo group]₀/[NaN₃]₀=1.0.

^bDetermined by size exclusion chromatography in CHCl₃ relative to poly(styrene)s.

^cDetermined by ¹H nuclear magnetic resonance spectrum.

^dDetermined by the second differential scanning calorimeter (DSC) scan at a heating rate of 10 °C min⁻¹.

^eDetermined by the first DSC scan at a heating rate of 10 °C min⁻¹.

Measurements

FT IR spectra were recorded using KBr disks on a JASCO FTIR-430 spectrometer (JASCO, Tokyo, Japan). The ^1H - and ^{13}C -NMR spectra were measured at 27 °C using a Bruker DPX200 (200 MHz) or a Bruker DRX600 (600 MHz) spectrometer (Bruker Biospin Corp., Billerica, MA, USA). All chemical shifts were expressed as downfield from tetramethylsilane (TMS) or 2,2-dimethyl-2-silapentane-5-sulfonate. The average molecular weights (M_n) and the polydispersity indices (M_w/M_n) of the polymers were estimated by size exclusion chromatography consisting of a Tosoh DP8020 pump fitted with an RI detector (Tosoh RI-8020, Tosoh Corp., Tokyo, Japan) and a TSK-GEL SuperMultipore HZ-M column (Tosoh Corp.) that was calibrated with polystyrene standards. The eluent used was chloroform, flow rate was 0.35 ml min^{-1} and the column temperature was maintained at 40 °C. The average molecular weights and the polydispersity indices of the polyesters (insoluble in chloroform) were estimated using another size exclusion chromatography system consisting of a Tosoh DP8020 pump system (Tosoh Corp.), a Tosoh RI-8020 differential refractometer, and Tosoh α -3000 and α -5000 TSK gel columns that were calibrated with polystyrene standards. The eluent used was 0.05 wt% LiBr in DMF, the flow rate was 0.5 ml min^{-1} , and the column temperature was maintained at 40 °C. All columns were obtained from the Tosoh Corp. The film surface was examined using a Hitachi S-2150 scanning electron microscope (Hitachi Ltd., Tokyo, Japan).

RESULTS AND DISCUSSION

Low-temperature polycondensation of dicarboxylic acids having bromo groups

The direct esterification of a dicarboxylic acid having pendent bromo groups (such as BSA or BAA) with a diol (such as 1,4-BD), as reported previously,⁶ occurred at 80 °C without dehydrobromination. To control the bromo content in the polyester, ternary polycondensations of BSA and 1,4-BD were carried out with MSA. The polycondensation reaction proceeded readily to generate polyesters having pendent bromo groups with M_n of 2.4×10^3 – 6.7×10^3 ($M_w/M_n=1.9$ – 2.2) with good yields. The observed ratio of BSA and MSA in the polyester as determined by the ^1H NMR was identical to that of the feed ratio.

Azidation of polyesters containing pendent bromo functionality using NaN_3

Results of the azidation of the polyesters having pendent bromo groups are shown in Table 1. First, azidation of poly(butylene bromosuccinate) (poly(BBS)) was carried out readily in DMF at room temperature using sodium azide (run 1 in Table 1). However, the resulting polyester was insoluble in any solvent even after a few days. The azido groups in this polyester seemed to have formed high-density crosslinked materials by the UV fraction of the visible light. To control the azide content in the polyester, we have carried out the polycondensation under low-light condition and demonstrated that the azidation of poly(butylene bromosuccinate-*co*-butylene methylsuccinate) (poly(BBS-*co*-BMS)) ([BSA]/[MSA]=1/4, mol/mol) proceeded to form azidopolyesters with $M_n=8.3 \times 10^3$ ($M_w/M_n=2.2$) (74% yield, run 5 in Table 1), which were soluble in chloroform. As expected, the IR spectrum of the resulting azidopolyesters shows a new absorption peak at 2106 cm^{-1} , a characteristic of the azido group (Figure 1). ^1H NMR analysis, however, showed 65% functionality, and revealed that the decreased functionality was due to the dehydrobromination (35%) that had occurred during the azidation. The produced maleate/fumarate units might have contributed to the dehydrobromination (Scheme 3).¹⁸

To optimize the experimental conditions, we next examined the effect of temperature on the azidation reaction (run 2–7 in Table 1). As the reaction temperature was raised ($>40\text{ °C}$), the azidation ratio is increased; however, the increased temperature is also known to cause crosslinks between the azide and double bond formation (data not shown) as the side reactions.¹⁹

Figure 1 Infrared spectrum of poly(butylene bromosuccinate-*co*-butylene methylsuccinate) (20 mol% of bromo content) after azidation.

Figure 2 ^1H nuclear magnetic resonance spectrum of poly(butylene azidoadipate) (in CDCl_3 , 27 °C, 200 MHz). DMF, *N,N*-dimethylformamide; TMS, tetramethylsilane.

On the other hand, as an example of the application of this procedure to non-conjugated substrates,¹⁸ we successfully carried out azidation of poly(butylene bromoadipate) (poly(BBA)) ($M_n=5.6 \times 10^3$ ($M_w/M_n=2.29$)) at room temperature for 1 h to generate poly(butylene azidoadipate) (poly(BAA)) (66% yield, $M_n=5.3 \times 10^3$ ($M_w/M_n=2.23$)) without any dehydrobromination and crosslinking (Figure 2), which was soluble in chloroform as shown in Table 2.

Copolyesters, in which the amount of BAA was controlled by ternally polycondensation with MSA ([BAA]/[MSA]=1/2 and 1/4, mol/mol, runs 2 and 3 in Table 2), were prepared and had $M_n=11.0 \times 10^3$ ($M_w/M_n=2.46$) and $M_n=10.4 \times 10^3$ ($M_w/M_n=2.25$). Subsequently, after azidation for 1 h, $>99\%$ bromo groups were converted into azido groups, as determined by ^1H NMR spectrum. After purification, the resultant azidopolyesters had an $M_n=10.4 \times 10^3$ ($M_w/M_n=2.71$) (49% yield, run 2 in Table 2), which were also soluble in chloroform. The reaction was carried out under mild conditions and proceeded in $>99\%$ azidation. M_n and M_w/M_n of the materials before and after azidation were hardly changed in the size exclusion

Scheme 3 A possible mechanism of dehydrobromination.

Figure 3 Scanning electron microscope image of photo-crosslinked poly(BBS-*co*-BMS) (20 mol% of bromo content) after ultraviolet irradiation.

chromatography measurements, indicating no side reaction during the azidation.

Photo-crosslinking of the azidopolyester by UV irradiation

First, poly(BAA) (run 1 in Table 2) was photo-crosslinked by UV irradiation with a high-pressure mercury lamp, which was insoluble in chloroform. As another example to demonstrate the photo-lithography that our materials afford, poly(butylene azidosuccinate-*co*-butylene methylsuccinate) (run 5 in Table 1) film prepared by spin-coating and prebaking was irradiated with a high-pressure mercury lamp through a negative photomask and then heated in an oven. The film was subsequently developed in CHCl_3 , which revealed a pattern (irradiated/non-irradiated part) successfully. Scanning electron microscope of the resulting pattern is shown in Figure 3. In a control experiment, the polyester having containing double bonds (poly(butylene fumalate-*co*-butylene methylsuccinate) ([FA]/[MSA]=1/4, mol/mol)) ($M_n=7.2 \times 10^3$ ($M_w/M_n=2.1$)) was irradiated under same condition, which was soluble entirely in chloroform even after the irradiation.

From these results, we confirmed that the pendent azido groups actually caused the crosslink under UV-irradiation.

Low-temperature polycondensation of dicarboxylic acid having hydroxyl groups

As another route to prepare azidopolyesters, direct polycondensation of L-TA and DEG, a reaction that was previously reported,⁸ proceeded at 80 °C without the formation of any crosslinks (reaction of secondary hydroxyl groups) to produce water-soluble poly(ester ether)s having pendent hydroxyl groups with M_n of 5.4×10^3 – 8.2×10^3 ($M_w/M_n=2.30$ – 2.86) as the prepolymers.

Azidation of polyesters containing pendent hydroxyl groups by using the DPPA–DBU method

Shioiri *et al.*¹⁶ have discovered that *p*-NO₂DPPA, prepared easily by nitration of DPPA,²⁰ in combination with DBU is quite useful and efficient in directly converting alcohols into azides. Following this protocol of the DPPA–DBU method, we converted the pendent hydroxyl groups of the polyesters into azides using *p*-NO₂DPPA and DBU. Poly(L-TA-*co*-DEG) was thus reacted with 50 mol% of *p*-NO₂DPPA and DBU in DMF at 50 °C for 22 h. The resulting azidopolyesters were repeatedly precipitated from the solution with tetrahydrofuran and then purified by dialyzing against water to remove the unreacted reagents, though removal of the byproducts of this reaction was difficult, thereby yielding the final product ($M_n=10.2 \times 10^3$, $M_w/M_n=4.27$) with 20% yield (run 1 in Table 3). The broad distribution in molecular weight of the resulting azidopolyesters is ascribed to the side reaction in which the carboxylic acid end-groups of the polyesters were directly converted to urethanes.²¹ This is because the reaction involves the formation of an unstable acyl azide from the carboxylic acid, followed by the Curtius rearrangement^{22–24} of the acyl azide to an isocyanate with the loss of a N₂ by heat. Subsequently, the urethanes are formed along with the alcohols.

To control the polyester end groups, therefore, polycondensation of L-TA and 1.05 equivalent mol of DEG was carried out at 80 °C for 12 h to produce polyesters having hydroxyl end groups with $M_n=5.4 \times 10^3$ ($M_w/M_n=2.30$) (59% yield after precipitation, run 3).^{4,8} We carried out azidation of the polyesters having pendent hydroxyl groups with 150 mol% of *p*-NO₂DPPA and DBU in DMF at room temperature for 12 h to readily generate polyesters having

Table 3 Azidations of polyesters having pendent hydroxyl groups by DPPA-DBU method^a

Run	L-TA/DEG Feed ratio	<i>p</i> -NO ₂ DPPA (mol%) ^d	DBU (mol%) ^d	Temp. (°C)	Time (h)	Yield (%)	$M_n^b \times 10^{-3} (M_w/M_n^b)$		Azidation ratio ^c (%)
							Before azidation	After azidation	
1	100:100	50	50	50	22	20 ^e	8.2 (2.86)	10.2 (4.27)	84
2	105:100	150	150	27	10	14 ^f	5.4 (2.30)	14.7 (1.62)	47
3	105:100	150	150	27	12	59 ^g	5.4 (2.30)	7.5 (2.25)	40

Abbreviations: DBU, 1,8-diazabicyclo[5.4.0]undec-7-ene; DEG, diethylene glycol; L-TA, L-tartaric acid; *p*-NO₂DPPA; bis(*p*-nitrophenyl) azidophosphonate.^aAll runs are performed by azidation in *N,N*-dimethylformamide (DMF), [polyester]₀=1.0 M in DMF (except for run 1: 0.5 M).^bDetermined by size exclusion chromatography measurement in DMF (0.05 wt% LiBr) relative to poly(styrene)s.^cDetermined by ¹H nuclear magnetic resonance spectrum ([azido groups]/[*p*-NO₂DPPA]₀).^dWith respect to hydroxyl group.^eAfter re-precipitation from DMF to tetrahydrofuran and dialysis against H₂O.^fThe reaction solution was dissolved in H₂O and filtrated. The isolated materials were re-precipitated from H₂O to acetone and dialyzed against H₂O.^gAfter re-precipitation from DMF to acetone and dialysis against H₂O. **Figure 4** Infrared spectra of poly(diethylene glycolyl L-tartrate) before (top) and after (bottom) azidation. **Figure 5** ¹H nuclear magnetic resonance spectrum for the poly(diethylene glycolyl L-tartrate) after azidation by the DPPA (diphenylphosphoryl azide)–DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) method (in dimethyl sulfoxide (DMSO)-*d*₆, 27 °C, 200 MHz). DSS, 2,2-dimethyl-2-silapentane-5-sulfonate. HOD, Hydrogen Oxygen Deuterium.

pendent azido groups with $M_n=7.5 \times 10^3$ ($M_w/M_n=2.25$) (59% yield, run 3 in Table 2). As expected, the IR spectrum showed a new absorption peak at 2126 cm^{-1} , a characteristic of the azido group (Figure 4). About 40% of the pendent hydroxyl groups were converted into azides as determined by ¹H NMR (Figure 5). This low azidation ratio seems to be ascribed to steric hindrance between the azido group and *p*-NO₂DPPA after azidation of one of the hydroxyl groups in L-TA unit occurred. Notably, the resultant azidopolyesters were also soluble in water, which is useful for lithography using aqueous media.

CONCLUSIONS

In this article, we described the syntheses of azidopolyesters by two methods. One strategy relies on the azidation of polyesters having pendent bromo groups using sodium azide without side reaction ($M_n > 1.0 \times 10^4$). Furthermore, we photo-crosslinked the azidopolyester by UV irradiation and examined it under scanning electron microscope. Another route involves azidation of polyesters having pendent hydroxyl groups by the DPPA–DBU method to synthesize water-soluble azidopolyesters with M_n of 7.5×10^3 ($M_w/M_n=2.25$). This azidopolyester could be used as a photolithography material that could use water as a developer. The polyesters developed in this study should provide valuable guideline for the design of advanced materials.

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