Synthesis and Thermal, Optical, and Mechanical Properties of Sequence-Controlled Poly(1-adamantyl acrylate)-*block*-Poly(*n*-butyl acrylate) Containing Polar Side Group

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ABSTRACT: We prepared the sequence-controlled block copolymers including poly(1-adamantyl acrylate) (PAdA) and poly(*n*-butyl acrylate) sequences as the hard and soft segments, respectively, by the organotellurium-mediated living radical polymerization. The thermal, optical, and mechanical properties of the adamantane-containing block copolymers with polar 2-hydroxyethyl acrylate (HEA) and acrylic acid (AA) repeating units were investigated. The microphase-separated structures of the block copolymers were confirmed by the differential scanning calorimetry and atomic force microscopy observations as well as dynamic mechanical measurements. The α - and β -dispersions due to the main-chain and side group

INTRODUCTION Adamantane (tricyclo[3.3.1.13,7]decane) is a unique compound that consists of fused cyclohexane rings with a fixed, highly symmetric, and thermodynamically stable structure the same as the diamond lattice, leading to characteristics such as a high melting point, reduced intermolecular interaction, a low friction coefficient, and high hydrophobicity.¹ A large variety of adamantane-containing polymers has been synthesized for use as thermoresistant polymers,²⁻⁵ rigid-chain polymers,⁶ high-performance membranes,⁷ dendritic polymers,⁸ photoresists,⁹ photoswitchable supramolec-ular hydrogels,¹⁰ unimolecular polymer micelles,¹¹ and hostguest materials.¹² Poly(methyl methacrylate) (PMMA) is one of the polymers with an excellent transparency and weather resistance, but its thermal stability is insufficient for use which requires a high-temperature resistance. Polymethacrylates including PMMA have a relatively rigid main chain and a low decomposition temperature as the intrinsic features of the poly(1,1-disubstituted ethylene)s, being in contrast to flexible polyacrylates as the typical soft materials with a low glass transition temperature (T_g) and a high decomposition temperature over 300 °C.¹³ Although conventional polyacrymolecular motions, respectively, of the hard and soft segments were observed. Their transition temperatures and activation energies increased due to the formation of intermolecular hydrogen bonding by the introduction of the HEA and AA repeating units. The effects of the hydrogen bonding on their tensile elasticity, strength, and strain were also evaluated. © 2014 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2014**, *52*, 2899–2910

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lates have been used as adhesives, paints, sealants, rubbers, and UV-curable resins, poly(1-adamantyl acrylate) (PAdA) exhibits a T_g value of 150 °C,^{3(a),3(b),14} which is high enough to be used as a thermoplastic material with an excellent thermal stability. High-temperature and transparent polymers have become more important for recent information and electronic technologies for optical disk, fiber, lens, display, digital signage, and lighting.¹⁵ In this study, we prepared the sequence-controlled block copolymers consisting of PAdA and poly(n-butyl acrylate) block sequences as the hard and soft segments, respectively, including polar repeating units by the organotellurium-mediated living radical polymerization¹⁶⁻¹⁹ (TERP). The TERP technique is one of the most powerful method for the controlled radical polymerization syntheses of high-molecular-weight polyacrylates containing a polar and functional side group.^{16,19} We investigated the thermal, optical, and mechanical properties of the acrylate block copolymers containing a bulky and hydrophobic adamantly moiety as well as a polar and functional moiety as new transparent acrylic polymers with a high $T_{\rm g}$.

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EXPERIMENTAL

General Procedures

The NMR spectra were recorded using Bruker AV300N and JEOL JNM-A400 spectrometers in CDCl₃. The number-average molecular weight (M_n) , weight-average molecular weight (M_w) , and polydispersity (M_w/M_n) were determined by size exclusion chromatography (SEC) in tetrahydrofuran (THF) as the eluent using a Tosoh CCPD RE-8020 system and calibration with standard polystyrenes. The atomic force microscopy (AFM) images were taken using a NanoScope IIIa system (Digital Instruments/Veeco) and an MMAFM-type Multimode SPM unit with a cantilever (OMCLAC240TS-C2, Olympus, spring constant 2.1-2.5 N/m, resonant frequency 73.4-77.6 kHz) at the scan rate of 0.5 Hz in the tapping mode for an area of 5 \times 5 μ m². The 2 wt % chloroform solutions of the polymers (ca. 1 μ L) were spin coated (250 rpm for 10 s and subsequent 2500 rpm for 40 s) on a glass plate $(1.2 \times 1.2 \text{ cm}^2)$, which were cleansed using acetone, 2-propanol under supersonic irradiation, then dried using an air duster. The film thickness was determined by scratching the films and measuring the step height between the glass and the film surface in the height mode. The water absorption property of the polymers was carried out at 23 °C using a test piece $(10 \times 10 \times 1 \text{ mm}^3)$, according JIS K7209. The amount of absorbed water was calculated based on a change in the polymer weight after immersion. The weight loss of the samples during immersion in water for a long time was corrected based on the weight of the dried samples.

Thermal Properties

The thermogravimetric and differential thermal analyses (TG/ DTA) were performed using a Seiko TG/DTA 6200 in a nitrogen stream (200 mL/min) at the heating rate of 10 °C/min in the temperature range of 30–500 °C. The onset temperature of decomposition was evaluated as the 5% weight-loss temperature (T_{d5}) in the TG analysis. The maximum temperature of decomposition (T_{max}) was determined using the derivatives of the TG curves. Differential scanning calorimetry (DSC) was performed in a nitrogen stream (50 mL/min) using a Seiko DSC-6200 at the heating rate of 10 °C/min in the temperature range of -100 to 200 °C to determine the T_g values.

Optical Properties

The UV–vis spectra were recorded using a JASCO V-550 spectrophotometer. The polymer films were prepared by casting of a 5 wt % chloroform solution and drying at 20 °C overnight. The refractive indices ($n_{\rm F}$, $n_{\rm D}$, and $n_{\rm C}$) were measured at the wavelengths of 486, 589, and 656 nm, respectively,²⁰ using an Abbe-type refractometer (Atago DR-M2, aqueous zinc dichloride saturated solution, halogen lamp). The average value of five measurements was typically recorded. The Abbe number ($v_{\rm D}$) was calculated as follows.

$$v_{\rm D} = \frac{(n_{\rm D} - 1)}{(n_{\rm F} - n_{\rm C})}.$$
 (1)

Mechanical Properties

The dynamic mechanical properties were determined using a Seiko DMS-6100 dynamic mechanical analyzer under atmos-

pheric conditions and temperature control. The measurements were performed using the flexural mode at frequencies of 0.5–10 Hz and the heating rate of 2 °C/min in the temperature range of -150 to 230 °C. The strain amplitude was 10 μ m. The apparent activation energy was evaluated for the relaxations using the peak tan δ temperatures and the applied frequency. The sample for the measurements was prepared using a dumbbell-type metal mold, AH-K1 (30 mm sample length, 5 mm width, 1.5 mm thickness for the narrow part), by compression of the polymer powders at the applied pressure of 10 MPa in vacuo at a temperature over each $T_{\rm g}$ for 2–3 h using an As-One AH2003 press machine. The tensile mechanical test was performed according to the standard test method using a universal testing machine, LSC-1/30 (JT Tone, Tokyo) with a 1 kN (at maximum) load cell at the rate of 1 mm/min at 20 °C. The tensile elasticity value was determined based on the initial slope of the curves in the stress-strain relationship (0.05-0.25% strain). The average value of the measurements for three samples was typically recorded except for the single datasets of some measurements. For preparing the cross-linked polymer sample for the dynamic mechanical measurements, the solution of tolylene diisocyanate (TDI, 0.169 mg, isocyanate content 0.137 mmol) and 3.5 g of PAdA43.7-b-P(AdA2.6/nBA47.3/ HEA_{6.4}) (hydroxy content 1.37 mmol) in 3 mL of toluene was cast on a Teflon plate and dried under atmospheric conditions to obtain polymer films containing TDI. The cut films were put in a dumbbell-type metal mold, and compressed under a load of 15 MPa at room temperature, then at 100 $^\circ$ C for 1 h. For the preparation of the thermally cross-linked test plates, the polymer powders were compressed at 200 °C under a load of 10 MPa in a metal mold, then at 240 °C for 2 h. The gel fraction was 79%.

Materials

Methyl acrylate (MA), n-butyl acrylate (nBA), tert-butyl acrylate (tBA), and 2-hydroxyethyl acrylate (HEA) were purchased from Tokyo Chemical Industry, Tokyo or Wako Pure Chemicals, Osaka, and distilled before use. 2,2'-Azobis(isobutyronitrile) (AIBN) and 2,2'-azobis(4-methoxy-2,4-dimethylvaleronitrile) (AMVN) were purchased from Wako Pure Chemicals, and recrystallized from methanol. All the solvents were used after distillation. Acryloyl chloride (Wako Pure Chemicals), 1-adamantanol (Sigma-Aldrich), triethylamine (TEA, Wako Pure Chemicals), benzenethiol (PhSH, Tokyo Chemical Industry, Tokyo), p-toluenesulfonic acid monohydrate (TsOH, 99.0%, Wako Pure Chemical Industries, Osaka), tolylene 2,4-diisocyanate (TDI, Tokyo Chemical Industry), and poly(methyl methacrylate) (PMMA, $M_{\rm n} = 6.33 \times 10^4$, $M_{\rm w}/M_{\rm n} = 1.84$, Wako Pure Chemical Industries, Osaka) were used as received. Ethyl 2-(n-butyltellanyl)-2-methylpropionate (BTEE, Otsuka Chemical, Tokushima, Japan) was used as received without further purification.

Synthesis of AdA

AdA was synthesized from acryloyl chloride and 1adamantanol. To the solution of 1-adamantanol (25 g, 164 mmol) and triethylamine (20 g, 198 mmol) in



SCHEME 1 Synthesis of block copolymers I with or without the HEA repeating unit [PAdA-*b*-P(AdA-*co*-nBA) and PAdA-*b*-P(AdA-*co*-nBA)] by TERP.

dichloromethane (400 mL), acryloyl chloride (24.7 g, 248 mmol) was dropwise added at 0 °C in an argon atmosphere. After the mixture was stirred at room temperature overnight, the resulting triethylamine hydrochloride as the precipitated salt was filtered out and the dichloromethane solution was washed with a saturated sodium bicarbonate, water, and a saturated saline solution, then dried over sodium sulfate. The dichloromethane was evaporated under reduced pressure, and the products were purified by silica gel chromatography using *n*-hexane and ethyl acetate (9:1 volume ratio). The isolated AdA was distilled under reduced pressure (115 °C/0.4 MPa) in the presence of catechol as the polymerization inhibitor, followed by passing through an alumina short column to completely remove the catechol.

AdA

Yield 50%; colorless crystals. M.p. 40.1 °C.

¹H NMR (CDCl₃, 300 MHz) δ 6.17 (dd, J = 1.6 and 17.3 Hz, 1H), 5.91 (dd, J = 10.3 and 17.3 Hz, 1H), 5.61 (dd, J = 1.6 and 10.3 Hz, 1H), 2.15 (br, 9H), 1.67 (br, 6H).

Polymerization

To a 15-mL glass tube, AMVN (0.72–1.49 mg) and a monomer (0.50–4.30 g) in 0.50–4.30 g of anisole were added and the solution was stirred with bubbling argon at 0 °C for 30 min, followed by the addition of BTEE (2.65–5.00 μ L) using a syringe. The polymerization was performed at 50 °C for 2 h. The conversion, M_n , and M_w/M_n values of the produced polymer were determined based on the NMR and SEC analyses of an aliquot. The block copolymerization was further performed at 50 °C for 2 h by the addition of the second monomer (1.00–3.39 g). After the block copolymerization, PhSH (0.33–3.70 μ L) and AIBN (0.38–0.79 mg) in 2.0–3.0 g of anisole were further added and heated at 80 °C for 5 h without isolating the produced block copolymers for the transformation of the polymer chain-end structure to the stable C-H one, then the final conversion was determined by ¹H NMR spectroscopy. The molar ratio of [AMVN]/[BTEE]/ [PhSH]/[AIBN] was always fixed at 0.2/1.0/1.5/0.2 in this study. The deactivated block copolymers were finally isolated in a large amount of methanol as the precipitant, then dried *in vacuo*. The block copolymers were characterized by ¹H NMR spectroscopy, SEC, and DSC measurements. For the synthesis of the block copolymers containing an acrylic acid repeating unit, the copolymerization was similarly performed using tBA instead HEA, then the tBA repeating unit included in the resulting block copolymers was hydrolyzed. To a 200mL flask, AdA-b-P(nBA/tBA) (4.2 g, tBA content 4.8-12.7 mol %) and TsOH (104 mg, 5.4×10^{-4} mol) in 100 mL of toluene were added, then refluxed for 5 h. The solution was poured into a large amount of methanol to precipitate the block copolymer. The copolymer was separated by filtration, then dried under reduced pressure overnight. After the reprecipitation, the quantitative transformation was confirmed by ¹H NMR spectroscopy and TG/DTA analyses.

RESULTS AND DISCUSSION

Synthesis of Block Copolymers

The block copolymers consisting of various PAdA and PnBA sequence structures were synthesized by the TERP method. After the first-step polymerization of AdA at 89–94% conversion, the block copolymerization of nBA or a nBA/HEA mixture was performed without isolating the precursor polymer (Scheme 1). Similarly, the AdA polymerization was performed in the presence or absence of HEA after the preparation of the precursor PnBA (Scheme 2). The results of the homo, random, and block polymerizations in the absence of a polar comonomer are summarized in Table 1. The results for the





SCHEME 2 Synthesis of block copolymers II with or without the HEA repeating unit [PnBA-*b*-P(nBA-*co*-AdA) and PnBA-*b*-P(nBA-*co*-AdA) and PnBA-*b*-P(nBA-*co*-AdA) by TERP.

preparation of the block copolymers containing polar HEA repeating units in either the hard or soft block segment are shown in Table 2. The produced block copolymers included a small amount of the AdA and nBA repeating units (0.4–3.6 mol %) in the second PnBA and PAdA sequences for the series of the block copolymers **I-x** and **II-x**, respectively. The letter *x* indicates the molar fraction of the AdA repeating units in the copolymers. In Table 2, the letters *x* and *y* indicate the molar fractions of the AdA and HEA repeating units, respectively, for **I-xHy** and **II-xHy**. Similarly, the letter *y* indicates the molar fractions of the tBA and AA repeating units for **I-xTBy**

and **I-xAy**, respectively. The alkyltellanyl group on the polymer chain end was converted to the stable C—H bond by the chain transfer reaction with benzene thiol (PhSH) at 80 °C for 5 h in the presence of AIBN before isolating the resulting polymers by a precipitation method.

The structure of the produced block copolymers was characterized by ¹H NMR spectroscopy and SEC measurements. The SEC peaks of the precursor PAdA and PnBA shifted to the higher molecular weight region while maintaining their narrow molecular weight distributions during the block

TABLE 1 Characterization of the Polymers without Polar Repeating Units Synthesized by TERP Method

		Conversion ^b (%)						
Polymer	Sequence Structure ^a	AdA	nBA	<i>M</i> _w ^b /10 ⁵	$M_{\rm w}/M_{\rm n}^{\rm b}$	<i>T</i> d₅ (°C)	<i>T</i> g [°] (°C)	% <i>T</i> ^d
PAdA	AdA homopolymer	96	_	2.31	1.48	358	156	92.8
PnBA	nBA homopolymer	-	93	1.61	1.19	346	-53	е
P(AdA/nBA)	P(AdA _{74.5} - <i>co</i> -nBA _{25.5}) [random]	90	94	2.87	1.85	364	25	е
I-33	PAdA _{31.9} - <i>b</i> -P(AdA _{0.9} - <i>co</i> -nBA _{67.2})	96(93)	92	1.44(0.79)	1.29(1.28)	359	-49, 145	е
I-53	PAdA _{50.4} - <i>b</i> -P(AdA _{2.1} - <i>co</i> -nBA _{47.5})	93(90)	88	1.86(1.22)	1.44(1.39)	343	-50, 151	92.8(90.9) ^f
l-53 ^g	PAdA _{50.4} - <i>b</i> -P(AdA _{2.1} - <i>co</i> -nBA _{47.5})							92.3(68.4) ^f
I-53M	PAdA _{51.3} - <i>b</i> -P(AdA _{1.5} - <i>co</i> -MA _{47.2})	96(94)	91	2.06(1.40)	1.44(1.33)	354	10, 149	92.0
II-64	PnBA _{32.1} - <i>b</i> -P(nBA _{3.6} - <i>co</i> -AdA _{64.3})	85	95(92)	1.45(0.45)	1.21(1.19)	378	-50, 127	92.5
II-75	PnBA _{24.3} - <i>b</i> -P(nBA _{0.4} - <i>co</i> -AdA _{75.3})	90	96(92)	1.60(0.38)	1.23(1.14)	360	-47, 133	91.1
II-79	PnBA _{18.1} - <i>b</i> -P(nBA _{3.0} - <i>co</i> -AdA _{78.9})	93	92(89)	2.36(0.26)	1.24(1.18)	361	-54, 137	92.1

^a The numbers in subscript denote the molar fraction of each monomer units.

^b Values in parentheses indicate those for the first-step polymerization.

^c Determined by DSC.

^d Transmittance at 380 nm.

^e Not determined.

 $^{\rm f}$ Values in parentheses indicate for the polymers after heating at 200 $^\circ \rm C$ for 2 h in air.

⁹ Butyltellanyl-terminated polymer without the postpolymerization reaction with PhSH.

TABLE 2 Characterization of Bloc	k Copolymers	Containing HEA and AA	Units Synthesized by	TERP Method
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	Conversion ^b (%)							
Sequence Structure ^a	AdA	nBA	HEA or tBA	<i>M</i> w ^b /10 ⁵	$M_{\rm w}/M_{\rm n}^{\rm b}$	<i>T</i> d₅ (°C)	T _{max} (°C)	<i>T</i> g ^c (°C)
PAdA _{43.4} - <i>b</i> -P(AdA _{1.7} - <i>co</i> -nBA _{50.1} - <i>co</i> -HEA _{4.8})	93(89)	87	90	2.04(1.54)	1.50(1.41)	340	407	-38, 152
PAdA _{43.7} - <i>b</i> -P(AdA _{2.6} - <i>co</i> -nBA _{47.3} - <i>co</i> -HEA _{6.4})	96(92)	91	86	2.53(1.67)	1.46(1.38)	342	411	-40, 149
PAdA _{43.7} - <i>b</i> -P(AdA _{2.6} - <i>co</i> -nBA _{47.3} - <i>co</i> -HEA _{6.4})						345	421	-38, 153
PAdA _{43.7} - <i>b</i> -P(AdA _{2.6} - <i>co</i> -nBA _{47.3} - <i>co</i> -HEA _{6.4})						344	418	-40, 154
PAdA _{42.8} - <i>b</i> -P(AdA _{5.3} - <i>co</i> -nBA _{44.2} - <i>co</i> -HEA _{7.7})	96(91)	90	88	2.36(1.58)	1.43(1.39)	343	406	-27, 152
PAdA _{42.6} - <i>b</i> -P(AdA _{2.9} - <i>co</i> -nBA _{40.8} - <i>co</i> -HEA _{13.7})	95(91)	88	88	2.34(1.38)	1.37(1.34)	349	407	-18, 149
PAdA _{75.3} - <i>b</i> -P(AdA _{6.2} - <i>co</i> -nBA _{13.0} - <i>co</i> -HEA _{5.5})	96(91)	86	84	2.31(1.84)	1.48(1.44)	343	420	10, 152
PnBA _{45.3} - <i>b</i> -P(nBA _{2.5} - <i>co</i> -AdA _{43.4} - <i>co</i> -HEA _{8.8})	89	93(89)	87	1.98(0.64)	1.34(1.25)	335	405	-50, 92
PAdA _{43.7} - <i>b</i> -P(AdA _{1.3} - <i>co</i> -nBA _{50.2} - <i>co</i> -tBA _{4.8})	92(90)	89	83	1.79(1.32)	1.26(1.26)	293	269, 414	
PAdA _{42.1} - <i>b</i> -P(AdA _{2.1} - <i>co</i> -nBA _{47.3} - <i>co</i> -tBA _{8.5})	93(91)	86	82	2.14(1.39)	1.33(1.20)	264	265, 414	
PAdA _{43.4} - <i>b</i> -P(AdA _{0.9} - <i>co</i> -nBA _{43.0} - <i>co</i> -tBA _{12.7})	90(90)	88	90	2.10(1.38)	1.29(1.24)	256	259, 402	
PAdA _{43.7} - <i>b</i> -P(AdA _{1.3} - <i>co</i> -nBA _{50.2} - <i>co</i> -AA _{4.8})						345	403	-25, 149
PAdA _{42.1} - <i>b</i> -P(AdA _{2.1} - <i>co</i> -nBA _{47.3} - <i>co</i> -AA _{8.5})						350	410	4, 153
PAdA _{43.4} - <i>b</i> -P(AdA _{0.9} - <i>co</i> -nBA _{43.0} - <i>co</i> -AA _{12.7})						342	418	36, 154
	Sequence Structure ^a PAdA _{43.4} -b-P(AdA _{1.7} -co-nBA _{50.1} -co-HEA _{4.8}) PAdA _{43.7} -b-P(AdA _{2.6} -co-nBA _{47.3} -co-HEA _{6.4}) PAdA _{43.7} -b-P(AdA _{2.6} -co-nBA _{47.3} -co-HEA _{6.4}) PAdA _{43.7} -b-P(AdA _{2.6} -co-nBA _{47.3} -co-HEA _{6.4}) PAdA _{43.7} -b-P(AdA _{2.6} -co-nBA _{47.3} -co-HEA _{6.4}) PAdA _{43.7} -b-P(AdA _{2.6} -co-nBA _{47.3} -co-HEA _{6.4}) PAdA _{42.8} -b-P(AdA _{2.9} -co-nBA _{44.2} -co-HEA _{7.7}) PAdA _{42.6} -b-P(AdA _{2.9} -co-nBA _{40.8} -co-HEA _{13.7}) PAdA _{45.3} -b-P(AdA _{6.2} -co-nBA _{13.0} -co-HEA _{8.8}) PAdA _{43.7} -b-P(AdA _{1.3} -co-nBA _{50.2} -co-tBA _{4.8}) PAdA _{43.4} -b-P(AdA _{0.9} -co-nBA _{43.0} -co-tBA _{4.8}) PAdA _{43.7} -b-P(AdA _{1.3} -co-nBA _{43.0} -co-AA _{8.5}) PAdA _{43.7} -b-P(AdA _{2.1} -co-nBA _{47.3} -co-AA _{8.5}) PAdA _{43.7} -b-P(AdA _{2.1} -co-nBA _{47.3} -co-AA _{8.5})	Con Sequence Structure ^a AdA PAdA _{43.4} -b-P(AdA _{1.7} -co-nBA _{50.1} -co-HEA _{4.8}) 93(89) PAdA _{43.7} -b-P(AdA _{2.6} -co-nBA _{47.3} -co-HEA _{6.4}) 96(92) PAdA _{43.7} -b-P(AdA _{2.6} -co-nBA _{47.3} -co-HEA _{6.4}) 96(92) PAdA _{43.7} -b-P(AdA _{2.6} -co-nBA _{47.3} -co-HEA _{6.4}) 96(92) PAdA _{43.7} -b-P(AdA _{2.6} -co-nBA _{47.3} -co-HEA _{6.4}) 96(91) PAdA _{42.6} -b-P(AdA _{2.9} -co-nBA _{44.2} -co-HEA _{7.7}) 96(91) PAdA _{42.6} -b-P(AdA _{2.9} -co-nBA _{41.3} -co-HEA _{5.5}) 96(91) PAdA _{42.6} -b-P(AdA _{2.9} -co-nBA _{41.3} -co-HEA _{5.5}) 96(91) PAdA _{43.7} -b-P(AdA _{2.9} -co-nBA _{41.3} -co-HEA _{5.5}) 96(91) PAdA _{43.7} -b-P(AdA _{2.1} -co-nBA _{41.3} -co-HEA _{5.5}) 90(90) PAdA _{43.7} -b-P(AdA _{2.1} -co-nBA _{41.3} -co-HEA _{6.8}) 91(91) PAdA _{43.7} -b-P(AdA _{2.1} -co-nBA _{41.3} -co-HA _{6.8}) 90(90) PAdA _{43.7} -b-P(AdA _{2.1} -co-nBA _{41.3} -co-HA _{6.8}) 90(90) PAdA _{43.7} -b-P(AdA _{2.1} -co-nBA _{41.3} -co-HA _{6.8}) 90(90) PAdA _{43.7} -b-P(AdA _{2.1} -co-nBA _{41.3} -co-HA _{6.8}) 90(90) PAdA _{43.7} -b-P(AdA _{2.1} -co-nBA _{41.3} -co-HA _{6.8}) 90(90) PAdA _{43.7} -b-P(AdA _{2.1} -co-nBA _{41.3} -co-HA _{6.8}) 90(90) PAdA _{43.7} -b-P(AdA _{2.1} -co-nBA _{4.3.0} -co	Conversion Sequence Structure ^a AdA nBA PAdA _{43.4} -b-P(AdA _{1.7} -co-nBA _{50.1} -co-HEA _{4.8}) 93(89) 87 PAdA _{43.7} -b-P(AdA _{2.6} -co-nBA _{47.3} -co-HEA _{6.4}) 96(92) 91 PAdA _{43.7} -b-P(AdA _{2.6} -co-nBA _{47.3} -co-HEA _{6.4}) 96(92) 91 PAdA _{43.7} -b-P(AdA _{2.6} -co-nBA _{47.3} -co-HEA _{6.4}) V V PAdA _{43.7} -b-P(AdA _{2.6} -co-nBA _{47.3} -co-HEA _{6.4}) V V PAdA _{42.6} -b-P(AdA _{2.6} -co-nBA _{44.2} -co-HEA _{6.4}) 96(91) 90 PAdA _{42.6} -b-P(AdA _{2.6} -co-nBA _{44.2} -co-HEA _{7.7}) 96(91) 88 PAdA _{43.7} -b-P(AdA _{2.6} -co-nBA _{44.2} -co-HEA _{7.7}) 96(91) 80 PAdA _{43.7} -b-P(AdA _{2.5} -co-AdA _{43.4} -co-HEA _{5.5}) 96(91) 81 PAdA _{43.7} -b-P(AdA _{2.1} -co-nBA _{50.2} -co-HEA _{5.5}) 91(91) 82 PAdA _{43.7} -b-P(AdA _{2.1} -co-nBA _{4.3.7} -co-HBA _{8.5}) 91(91) 83 PAdA _{43.7} -b-P(AdA _{2.1} -co-nBA _{4.3.7} -co-AA _{4.8}) 91(91) 82 PAdA _{43.7} -b-P(AdA _{2.1} -co-nBA _{4.3.7} -co-AA _{4.8}) 91(91) 83 PAdA _{43.7} -b-P(AdA _{2.1} -co-nBA _{4.3.7} -co-AA _{4.8}) 91(91) 82 PAdA _{43.7} -b-P(AdA _{2.1} -co-nBA _{4.3.7} -co-AA _{4.8})	Conversion Conversion Requence Structure ^a AdA nBA BAA PAdA43.4-b-P(AdA1.7-co-nBA60.1-co-HEA4.0 93(89) 97.0 93(80) 91.0 93(80) PAdA43.7-b-P(AdA2.6-co-nBA47.3-co-HEA4.0) 96(92) 91.0 86 91.0	Co	CONVERSION CONVERSION REA REA REA Sequence Structure ^a AdA nBA RBA Mw ^b 10 ⁵ Mw/M ^b PAdA _{43.4} -b-P(AdA _{1.7} -co-nBA _{50.1} -co-HEA _{4.8} 93(89) 87 90 2.04(1.50) 1.50(1.41) PAdA _{43.7} -b-P(AdA _{2.6} -co-nBA _{4.7.3} -co-HEA _{6.4} 96(92) 91 86 2.53(1.67) 1.46(1.38) PAdA _{43.7} -b-P(AdA _{2.6} -co-nBA _{4.7.3} -co-HEA _{6.4} V V V V V PAdA _{43.7} -b-P(AdA _{2.6} -co-nBA _{4.7.3} -co-HEA _{6.4} V V V V V PAdA _{43.7} -b-P(AdA _{2.6} -co-nBA _{4.7.3} -co-HEA _{6.4}) 910 81 2.30(1.58) 1.43(1.39) PAdA _{42.6} -b-P(AdA _{2.6} -co-nBA _{4.6.2} -co-HEA _{1.5}) 9101 81 81 2.31(1.84) 1.31(1.34) PAdA _{4.5.6} -b-P(AdA _{2.6} -co-nBA _{4.6.6} -co-HEA _{1.5}) 9101 81 81 1.31(1.34) 1.34(1.34) PAdA _{4.5.7} -b-P(AdA _{2.5} -co-ABA _{4.5.6} -co-HEA _{6.5}) 9101 81 81 1.31(1.34) 1.34(1.34) PAdA _{4.5.7} -b-P(AdA _{2.5} -co-ABA _{4.5.6} -co-HEA _{6.5}) 910 81 91	$\begin{array}{ c c c c } & \hline \\ \hline$	$\begin{split} $

^a The numbers in subscript denote the molar fraction of each monomer units.

^b Values in parentheses indicate those for the first-step polymerization.

copolymerization (Fig. 1). The M_w and M_w/M_n values of the polymers are shown in Tables 1 and 2, together with the T_{d5} , T_{max} , and T_{g} values as well as the transmittance of light at 380 nm. The block copolymers exhibited high T_{d5} and $T_{\rm max}$ values, which were over 340 and 400 °C, respectively, independent of the composition and the structure of the polar repeating units due to the excellent thermal stability of the polyacrylate main chain and the adamantyl ester group. The synthetic path shown in Scheme 1 was preferred for the production of the block copolymers with a constant $T_{\rm g}$ value for the PAdA segment at about 150 °C. In contrast, the reaction process according to Scheme 2 provided the block copolymers containing the hard segment with lower $T_{\rm g}$ values (92-137 °C), which depended on the composition of the repeating units in the hard segment. The films of PAdA and the block copolymers obtained by casting the polymer solutions exhibited high transparency of visible light with over a 90% transmittance at 380 nm. The copolymers including the butyltellanyl group at the chain end without a postpolymerization process to obtain the stable C-H chain end become colored after heating at 200 °C for 2 h in air and the transmittance value decreased to 68%. In contrast, the postpolymerization chain-end transformation by PhSH in the presence of AIBN for removing the terminal telluride moiety produced thermally stable transparent copolymers; no change in the transmittance value occurred before and after the heating (see Table 1).

We also synthesized the block copolymers containing a carboxylic acid as the alternative polar repeating unit. To synthesize polymers containing a carboxylic acid in the side group during the living radical polymerization, the use of a protected mono^c Determined by DSC.

^d After thermal curing with TDI at 100 $^{\circ}$ C for 1 h.

^e After thermal curing without TDI at 240 °C for 2 h.

mer is valid to avoid a less-controlled polymerization and precipitation of the copolymers during the polymerization. The polymers including tert-butyl acrylate (tBA) as the repeating unit are readily converted to the polymers containing acrylic acid (AA) repeating units via postpolymerization reactions.²¹ In this study, AdA was first polymerized, then nBA and tBA were copolymerized (Scheme 3). After the polymerization, the isolated PAdA-b-P(AdA-co-nBA-co-tBA)s (I-xTBy) were transformed to PAdA-b-P(AdA-co-nBA-co-AA)s (I-xAy) by an acidcatalyzed reaction. The process of transformation was monitored by TG/DTA, IR, and NMR spectroscopies. The TG themogram of the polymers containing a *tert*-butyl ester in the side group exhibited the characteristic decomposition behavior, which included the reaction steps of elimination of the isobutene and the decomposition of the resulting carboxylic acid polymers at a higher temperature (Fig. 2). The weight loss of the block copolymers containing the tBA repeating units started from 250 °C and the magnitude of weight loss increased according to the content of the tBA units in the copolymers. No weight loss due to the isobutene elimination was observed in the TG curve of the PAdA-b-P(AdA-co-nBA-co-AA), indicating that the chemical transformation totally occurred. The quantitative transformation was also confirmed based on the fact that the peak due to the tert-butyl group was not detected in the ¹H NMR spectrum after the side-chain transformation. The $T_{\rm g}$ due to the PnBA soft segment including the AdA and AA repeating units was observed in the range of -25 to 36 °C after the transformation reaction. The T_{g} value of the soft segment in the PAdA-b-P(AdA-co-nBA-co-AA)s increased with an increase in the AA content, while no change was observed in the $T_{\rm g}$ value of the PAdA segment.





FIGURE 1 SEC curves for precursor polymers (dotted) and block copolymers (solid); (a) I-48H8, (b) II-43H9, and (c) I-44TB9. See Table 2 for the detailed structures of the block copolymers.

Microphase-Separated Structure

The block copolymers exhibited two $T_{\rm g}$ values corresponding to the hard and soft segments, as shown in the DSC thermograms in Figure 3. This was due to the formation of a microphase-separated structure. The $T_{\rm g}$ values of the PAdA segments were as high as 145-151 °C. The PAdA sequences including a small amount of the nBA repeating unit exhibited lower T_g values (127–133 °C). The soft segments exhibited $T_{\rm g}$ values in a wide range according to the sequence structures. The $T_{\rm g}$ values of the PnBA soft segments increased in the polar repeating units due to the intermolecular interactions between the hydroxy and carboxy groups. Conversely, the introduction of the HEA units into the hard PAdA segments decreased the $T_{\rm g}$ values to 92 °C, as seen in the result for the block copolymer, II-43H9, of which the PAdA hard segments contained a small amount of nBA and HEA repeating units (see Table 2).

Figure 4 shows phase images for the AFM observations of the spin-coated film surfaces of the block copolymer containing different amounts of the HEA units. The block copolymers of PAdA and PnBA with the 1:1 composition including no HEA unit (**I-53**) exhibited a lamella structure, as shown in Figure 4(a). A similar lamella structure was also observed for **I-48H5** including 4.8 mol % of the HEA unit. The island structure was more clearly observed for **I-46H14** including a higher amount of HEA in the soft segment. This island structure corresponding to the component with a small phase delay was assigned as the PAdA hard segment. The reverse image consisting of the soft segment as the island and the PAdA continuous phase was observed for **I-82H6**, of which the AdA content was 75.3 mol % in the hard segment [Fig. 4(d)].

Optical Property

The copolymers were soluble in organic solvents, such as toluene, chloroform, 1,2-dichloroethane, and THF, and the



SCHEME 3 Synthesis of block copolymers with the AA repeating unit [PAdA-b-P(AdA-co-nBA-co-AA)] by TERP.



FIGURE 2 TG curves for (a) PAdA-*b*-P(AdA-*co*-nBA-*co*-tBA)s (**I**-45TB5, **I**-45TB9, and **I**-45TB13) and (b) PAdA-*b*-P(AdA-*co*-nBA-*co*-AA)s (**I**-45A5, **I**-45A9, and **I**-45A13) at the heating rate of 10 °C/min in a nitrogen stream. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

transparent films were obtained by casting the solutions. The block copolymers were highly transparent as well as PAdA and the other polymethacrylates including PMMA and poly(1-adamantyl methacrylate).²² The transmittance of visible light (at 380 nm) was more than 90% for the block copolymers. The microphase separated structure of the copolymers did not influence the scattering of light due to a domain size smaller than the wavelength of the light and similar reflective index values for the PAdA and PnBA segments. The n_D and v_D values were in the ranges of 1.491-1.492 and 45-47, respectively, for both the PAdA and PAdA*b*-PnBAs. The n_D values slightly increased to 1.492–1.494 and the $v_{\rm D}$ values decreased to 42–45 by the introduction of the HEA units into the block copolymers. The magnitude of the change in the $n_{\rm D}$ and $v_{\rm D}$ values depended on the HEA content. The introducton of the AA unit into the copolymers provided simialr results; a high $n_{\rm D}$ value and a low $v_{\rm D}$ value were observed for I-45A5. The films of the copolymers containing an amount greater than 8.5 mol % as the repeating unit (I-44A9 and I-44A13) were brittle and their optical parameters other than the transmittance values were not determined in this study.

The amount of absorbed water by PAdA was lower than that of PMMA, as shown in Table 3. The block copolymers with

no polar substituents, PAdA-b-PnBA, exhibited a low water absorption property similar to that of the PAdA homopolymer. The introduction of the HEA unit increased the amount of the absorbed water according to the amount of the introduced HEA unit in the copolymers (Fig. 5). The polymers containing a hydroxy group in the side chain tended to imply water in the hydrophilic domain formed by the aggregation of the hydroxy units, as shown in the poly(2-hydroxyethyl methacrylate) and the N-(hydroxyalkyl)maleimide-olefin copolymers.²³ Conversely, a carboxylic acid moiety readily dimerizes to form its robust dimer by strong hydrogen bonding without any participation by the water molecules. As a result, the water absorption amount for the block copolymers containing AA repeating units was low due to the excellent hydrophobic property of the adamantyl group compared to that for PMMA.

Dynamic Mechanical Property

The viscoelastic properties of the block copolymers with different repeating structures were investigated by the dynamic mechanical analysis in the flexural mode at the frequencies of 0.5–10 Hz in the range of -150 °C to a temperature over the $T_{\rm g}$ values at the heating rate of 2 °C/min. The temperature dependences of the storage modulus (E') and tan δ values for I-46H14 are shown in Figure 6. The results for the other block copolymers and PAdA are summarized in Table 4, together with the apparent activation energies (E_{act}) , which were calculated based on the plots of the tan δ values as a function of the temperature. High tan δ peaks were observed in the temperature range of 172-221 °C, which corresponded to the glass transition of the hard segment of the block copolymers. Weaker tan δ peaks were also detected in the range of -50 to -4 °C, which corresponded to the glass transition of the soft segment. Broad and weak β -dispersions were also observed due to the side-chain dynamics in the temperature range lower than -80 °C.²⁴ The high and constant E_{act} values (275–294 kJ/mol) were observed for the glass transition motion of the hard PAdA



FIGURE 3 DSC curves for homopolymers (a) **PnBA** and (b) **PAdA**, and block copolymers (c) **I-45H5**, (d) **I-46H14**, and (e) **I-53M** at the heating rate of 10 °C/min. See Tables 1 and 2 for the structures of the polymers.



FIGURE 4 AFM observations of microphase separated structures of the block copolymers. (a) I-53, (b) I-48H5, (c) I-46H14, and (d) I-82H6. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

segment for all the block copolymers. This was due to the repeating unit structure of the hard segment, which exclusively consisted of the AdA repeating unit without incorporating any other monomer units such as nBA, HEA, and AA. The E_{act} value for the block copolymers including the HEA

TABLE 3 Optical and Water Absorption Properties of the Block

repeating units in their soft segments were higher than those of the copolymers including no HEA units and the values increased in the order of I-45H5 < I-48H8 < I-46H14 due to the intermolecular hydrogen bonding between the

Copolymers									
Polymer	Transmittance at 380 nm	n _D	vD	Absorbed Water ^a (%)					
PAdA	92.8	1.4913	45.3	0.42					
I-53	92.8	1.4915	46.5	0.41 ^b					
I-45H5	92.4	1.4918	45.0	0.55					
I-48H8	91.4	1.4923	44.1	0.65					
I-46H14	90.7	1.4943	42.3	0.75					
I-45A5	92.6	1.5026	42.1	0.42					
I-44A9	91.0	С	с	0.46					
I-44A13	89.7	с	С	0.51					

1.4916

0.66

54.3

94.0 ^a After at room temperature for 72 h.

^b After 48 h.

PMMA

^c Not determined.



FIGURE 5 Water absorption property of the block copolymers with the (\bigcirc) HEA and (\triangle) AA repeating units. The water absorption ratio increased with an increase in the content of the polar repeating units (see Table 3).



FIGURE 6 Temperature dependence of (a) storage modulus (*E*), and loss modulus (*E'*), (b) tan δ values for **I-46H14** determined by dynamic mechanical measurement at frequencies of 0.5, 1, 2, 5, and 10 Hz. (c) Expansion of the data of tan δ in the low temperature region. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

hydroxy moieties. It is also noted that the $E_{\rm act}$ value for **I**-**53M** was higher than that for **I-53** due to a difference in the chain flexibility of the soft segment. These results were the same as the order for the peak temperatures of the tan δ by viscoelastic measurements and agreed well with the $T_{\rm g}$ behaviors evaluated by DSC.

Tensile Mechanical Property

The tensile test was performed at 20 $^\circ\text{C}$ and tensile elasticity was determined based on an initial stress-strain relation-

ship. All the samples showed nonductile fracture without necking except for the random copolymer, P(AdA/nBA), which had a low elasticity and was not broken even after an elongation over 10%. The block copolymers showed tensile elasticity values similar to that of PAdA due to the PAdA domain as the continuous phase for the copolymers I-53 and II-75 with the PAdA content over 60 wt %. The high elasticity of PAdA as the matrix was reflected in all the mechanical characteristics of the block copolymers. Conversely, the maximum tensile strength and strain values of the block copolymers were lower than those of PAdA; for example, the maximum tensile strength values were 2.8-8.9 MPa and the maximum tensile strain values were 0.4-0.9% for the block copolymers, being much lower than those for PAdA; 14.3 MPa and 1.5% (Fig. 7). This is due to the reduced area of the cross section of the hard segment, resulting in a decreased mechanical toughness. The block copolymer including the soft segment with a high T_{g} , that is, I-53M with the $T_{\rm g}$ value of 10 °C for the soft segment, showed high elasticity, tensile strength, and strain values compared to those of I-53, as shown in Table 5. This supported that the mechanical failure was induced by the plastic deformation of the soft domain.

The effect of the introduction of the HEA and AA repeating units as the polar groups in the side chain on the mechanical properties was investigated (Fig. 8). The maximum tensile strength and strain values increased four to five times by the introduction of the HEA units into the soft segment. The maximum tensile strain of I-46H14 was 2.4%, which is 1.6 times greater than that of PAdA. No increment in the mechanical strength was observed when the HEA units were introduced in the hard segment, as seen in the results for II-43H9. Similarly, I-44A9 exhibited the highest tensile strength and strain values when the properties were compared among the block copolymers containing a different amount of the AA unit. The enhancement effect of the strength of the AA unit was greater than that of HEA units due to the robust intermolecular hydrogen bonding between two carboxylic acid groups. This is due to the high $T_{\rm g}$ value of I-44A13. When the content of the AA units in the soft segment further increased from 8.5 to 12.7 mol %, the maximum tensile strength and strain values were reduced. This is due to the change in the $T_{\rm g}$ of the soft segments; -25, 4, and 36 °C for the block copolymers containing the AA units

TABLE 4 Dynamic Mechanical Property of the Block Copolymers at a Frequency of 1 Hz in the Flexural Mode

		tan δ	Peak Tem	perature (°C)	1	an δ Peak	Intensity	E _{act} (kJ/mol) (0.5–10 Hz)
Polymer	<i>E</i> ′ (20 °C) (GPa)	α1	α2	β	α1	α2	β	α1	α2	β
PAdA	1.03	183		-96	79.1		0.039	292		
I-53	0.85	172	-51	-95	92.9	0.057	0.059	275	210	
I-53M	0.79	196	-11	-85	97.4	0.098	0.088	294	236	
I-45H5	1.05	198	-7	-82	59.6	0.061	0.050	279	239	152
I-48H8	0.86	198	-6	-80	41.2	0.091	0.045	287	257	147
I-46H14	1.01	221	-4	-89, -109	44.0	0.122	0.059, 0.059	287	272	130, 113





FIGURE 7 Stress-strain curves for (a) homopolymer (**PAdA**), random copolymer [**P(AdA/nBA**)], and block copolymers (**I-53, II-64**, and **II-75**) and (b) bock copolymer including a polar group before and after cross-linking (**I-46H6** and **I-46H6-X**). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

with 4.8, 8.5, and 12.7 mol %, respectively. Because the mechanical strength tests were performed at room temperature, the I-44A13 sample that included both block sequences in the glassy state exhibited a more fragile failure behavior compared to I-43A9. In this study, the higher toughness of the block copolymers containing the HEA units was further examined by the introduction of a cross-linking structure. The cross-linking reaction was performed in the presence of diisocyanate (TDI) as the cross-linker (see data for I-46H6-X in Tables 2 and 5). As a result, the maximum tensile strength and strain values reached 25 MPa and 3.2% which were 1.5-2 times greater than those before the cross-linking. Similar enhanced mechanical properties were also observed by the thermally cured polymers without any cross-linker at 240 °C for 2 h. No change was observed for the $T_{\rm g}$ value determined by DSC during the cross-linking reaction (Table 2), while the

transmittance of light at 380 nm decreased to about 70% after the TDI cross-linking.

CONCLUSIONS

Transparent polymers with high $T_{\rm g}$ values and excellent mechanical properties are some of key materials for electronic and photonic applications. Several materials consisting of components with different physical properties, such as organic-inorganic composites using nanoparticles, thermoplastic elastomers, fiber reinforced composites, and bicontinexhibited excellent uous network structures, an transparency, low birefringence, and low water absorption as well as a high thermal resistance.¹⁵ Another simple method for the fabrication of high $T_{\rm g}$ and transparent polymers is the introduction of a bulky substituent in the side group of

Polymer	Tensile Elasticity (GPa)	Maximum Tensile Strength (MPa)	Maximum Tensile Strain (%)
PAdA	1.13	14.3	1.47
P(AdA/nBA)	0.13	No breaking	No breaking
I-53	0.71	2.8	0.39
I-53M	1.03	6.8	0.69
II-75	0.99	8.9	0.92
I-45H5	0.66 ± 0.04	9.7 ± 0.2	1.55 ± 0.1
I-46H6	0.69	10.9	2.05
I-46H6-X ^a	0.88	24.8	3.19
I-46H6-X [♭]	1.04	25.7	2.67
I-48H8	0.66 ± 0.05	11.5 ± 1.7	2.11 ± 0.4
I-46H14	0.70 ± 0.05	12.7 ± 0.3	2.37 ± 0.2
II-43H9	0.45 ± 0.04	3.5 ± 1.0	0.97 ± 0.4
I-45A5	0.69 ± 0.04	11.2 ± 0.2	1.77 ± 0.1
I-44A9	0.70 ± 0.01	16.3 ± 0.5	2.62 ± 0.1
I-44A13	0.71 ± 0.03	13.5 ± 1.1	2.06 ± 0.1

TABLE 5 Tensile Mechanical Property of the Block Copolymers

 $^{\rm a}$ After thermal curing with TDI at 100 $^{\circ}{\rm C}$ for 1 h.

 $^{\rm b}$ After thermal curing without TDI at 240 $^{\circ}\text{C}$ for 2 h.



FIGURE 8 The effect of the HEA and AA contents in the block copolymers on their tensile mechanical elasticity, maximum tensile strength, and maximum tensile strain values. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the acrylic polymers,²⁵ because the mechanical property of the acrylic polymers can be controlled over a wide range of elasticity values (0.01-1 GPa) depending on the structure of the side groups. In this study, we have demonstrated that the acrylate block copolymers containing the adamantyl moiety exhibited an excellent thermal stability, such as high decomposition and glass transition temperatures, and the high transmittance of visible light. The mechanical strength of the block copolymers consisting of the PAdA and PnBA sequences as the hard and soft segments, respectively, was modified by the introduction of polar groups such as the HEA and AA repeating units. The PAdA-b-(PnBA-co-HEA)s and the PnBA-b-(PAdA-co-HEA)s produced by the TERP method, as one of the controlled living radical polymerization processes, had an excellent transparency and the former was superior to the latter due to the constant $T_{\rm g}$ values and tensile elasticity independent of the amount of HEA units introduced in the soft segment. The increase in the introduced HEA and AA units induced an increase in the tensile strength. The dynamic mechanical analysis revealed that the activation energies for the soft segment motion were increased by hydrogen bonding between the HEA units. The cross-linking of the HEA-containing block copolymers by the

reaction of diisocyanate led to the further enhancement of the maximum mechanical strength and elongation values, as expected. The living radical polymerization includes several features superior to the living anionic polymerization, such as a tolerance to polar and functional groups, the formation of random and alternating copolymer sequences, the possibility of various polymer sequence designs, and so forth.²⁶ We have demonstrated that the TERP method is valid for the synthesis of polyacrylate block copolymers with wellcontrolled sequence structures including polar side groups, and that the combination of bulky cycloalkyl substituents in the side groups with the controlled polymerization technique provides various kinds of high-performance transparent polymers, which will be useful for electronic and photonic technologies in the future.

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REFERENCES AND NOTES

1 (a) R. C. Font, Jr., P. v. R. Schleyer, *Chem. Rev.* **1964**, *64*, 277–300; (b) R. C. Bingham, P. v. R. Schleyer, *Top. Curr. Chem.* **1971**, *18*, 1–102; (c) H. Schwertfeger, A. A. Fokin, P. R. Schreiner, *Angew. Chem., Int. Ed.* **2008**, *47*, 1022–1036.

2 (a) H. F. Reinhardt, Polym. Lett. 1964, 2, 567-568; (b) S. Moon, A. L. Schwartz, J. K. Hecht, J. Polym. Sci., Part A-1: Polvm, Chem, 1970, 8, 3665–3666; (c) S. Nozakura, T. Okamoto, K. Toyora, S. Murahashi, J. Polym. Sci., Polym. Chem. Ed. 1973, 11, 1043-1051; (d) J. C. Wilson, J. Polym. Sci., Polym. Chem. Ed. 1976, 14, 2927–2940; (e) Y. Okano, T. Masuda, T. Higashimura, J. Polym. Sci., Polym. Chem. Ed. 1985, 23, 2527-2537; (f) B. R. Hsieh, M. H. Litt, J. Polym. Sci., Part A: Polym. Chem. 1988, 26, 2501-2515; (g) Y. T. Chern, W. H. Chung, J. Polym. Sci., Part A: Polym. Chem. 1996, 34, 117-124; (h) S. H. Hsaiao, C. T. Li, Macromolecules 1998, 31, 7213-7217; (i) H. Seino, A. Mochizuki, M. Ueda, J. Polym. Sci., Part A: Polym. Chem. 1999, 37, 3584-3590; (j) J. F. Espeso, J. G. de la Campa, A. E. Lozano, J. de Abajo, J. Polym. Sci., Part A: Polym. Chem. 2000, 38, 1014-1023; (k) D. J. Liaw, B. Y. Liaw, Polymer 2001, 42, 839-845; (I) C. Sinkel, S. Agarwal, N. A. Fokina, P. R. Schreiner, J. Appl. Polym. Sci. 2009, 114, 2109–2115; (m) K. Fuchise, M. Sone, Y. Miura, R. Sakai, A. Narumi, S. Sato, T. Satoh, T. Kakuchi, Polym. J. 2010, 42, 626-631; (n) T. Imaeda, T. Hashimoto, S. Irie, M. Urushisaki, T. Sakaguchi, J. Polym. Sci., Part A: Polym. Chem. 2013, 51, 1796-1807; (o) K. Morita, T. Hashimoto, M. Urushisaki, T. Sakaguchi, J. Polym. Sci., Part A: Polym. Chem. 2013, 51, 2445-2454.

3 (a) A. Matsumoto, S. Tanaka, T. Otsu, *Macromolecules* **1991**, *24*, 4017–4024; (b) T. Otsu, A. Matsumoto, A. Horie, S. Tanaka, *Chem. Lett.* **1991**, 1145–1148; (c) A. Matsumoto, A. Horie, T. Otsu, *Makromol. Chem., Rapid Commun.* **1991**, *12*, 681–685; (d) A. Matsumoto, H. Watanabe, T. Otsu, *Bull. Chem. Soc. Jpn.* **1992**, *65*, 846–852; (e) A. Matsumoto, K. Shimizu, K. Mizuta, T. Otsu, *J. Polym. Sci., Part A: Polym. Chem.*, **1994**, *32*, 1957–1968.



4 (a) V. R. Reichert, L. J. Mathias, *Macromolecules* **1994**, *27*, 7015–7023; (b) C. C. Cypcar, P. Camelio, V. Lazzeri, L. J. Mathias, B. Waegell, *Macromolecules* **1996**, *29*, 8954–8959; (c) L. J. Mathias, C. M. Lewis, K. N. Wiegel, *Macromolecules* **1997**, *30*, 5970–5975; (d) H. Y. Acar, J. J. Jensen, K. Thigpen, J. A. McGowen, L. J. Mathias, *Macromolecules* **2000**, *33*, 3855–3859.

5 (a) T. Ishizone, H. Tajima, H. Torimae, S. Nakahama, *Macromol. Chem. Phys.* **2002**, *203*, 2375–2375; (b) S. Inomata, S. Matsuoka, S. Sakai, H. Tajima, T. Ishizone, *Macromolecules* **2012**, *45*, 4184–4195; (c) S. Inomata, Y. Harada, Y. Nakamura, Y. Uehara, T. Ishizone, *J. Polym. Sci., Part A: Polym. Chem.* **2013**, *51*, 4111–4124.

6 (a) A. Matsumoto, S. Tanaka, T. Otsu, *Colloid Polym. Sci.* **1992**, *270*, 17–21; (b) A. Matsumoto, T. Otsu, *Chem. Lett.* **1991**, 1361–1364.

7 (a) M. R. Pixton, D. R. Paul, *Polymer* **1995**, *36*, 3165–3172; (b) H. Lim, M.-C. Cha, J.-Y. Chang, *Polym. Chem.* **2012**, *3*, 868–870; (c) S. Kanehashi, S. Konishi, K. Takeo, K. Owa, H. Kawakita, S. Sato, T. Miyakoshi, K. Nagai, *J. Membrane Sci.* **2013**, *427*, 176–185; (d) H. Kim, M.-C. Cha, H.-W. Park, J.-Y. Chang, *J. Polym. Sci., Part A: Polym. Chem.* **2013**, *51*, 5291–5297.

8 G. R. Newkome, A. Nayak, R. K. Behera, C. N. Moorefield, G. R. Baker, *J. Org. Chem.* **1992**, *57*, 358–362.

9 (a) D. Pasini, E. Low, J. M. J. Fréchet, *Adv. Mater.* **2000**, *12*, 347–351; (b) C. K. Ober, K. Douki, V. R. Vohra, Y. J. Kwark, X. Q. Liu, W. Conley, D. Miller, P. Zimmerman, *J. Photopolym. Sci. Technol.* **2002**, *15*, 603–611; (c) T. Ogata, S. Matsumaru, H. Shimizu, N. Kubota, H. Hada, M. Shirai, *J. Photopolym. Sci. Technol.* **2004**, *17*, 483–488; (d) K. Nozaki, *J. Photopolym. Sci. Technol.* **2010**, *23*, 795–801; (e) S. Fleischmann, V. Percec, *J. Polym. Sci., Part A: Polym. Chem.* **2010**, *48*, 2251–2255; (f) H.-S. Sohn, S.-H. Cha, W.-K. Lee, D.-G. Kim, H.-J. Yun, D.-B. Kim, J.-H. Kim, J.-C. Lee, *Macromol. Res.* **2011**, *19*, 722–728.

10 (a) O. Kretschmann, S. W. Choi, M. Miyauchi, I. Tomatsu, A. Harada, H. Ritter, *Angew. Chem., Int. Ed.* **2006**, *45*, 4361–4365; (b) P. Kuad, A. Miyawaki, Y. Takashima, H. Yamaguchi, A. Harada, *J. Am. Chem. Soc.* **2007**, *129*, 12630–12631; (c) S. Tamesue, Y. Takashima, H. Yamaguchi, S. Shinkai, A. Harada, *Angew. Chem., Int. Ed.* **2010**, *49*, 7461–7464.

11 Y. Morishima, S. Nomura, T. Ikeda, M. Seki, M. Kamachi, *Macromolecules* **1995**, *28*, 2874–2881.

12 (a) S. H. Pun, N. C. Bellocq, A. J. Liu, G. Jansen, T. Machemer, E. Quijano, T. Schluep, S. F. Wen, H. Engler, J. Heidel, M. E. Davis, *Bioconjug. Chem.* 2004, *15*, 831–840; (b) K. Ohga, Y. Takashima, H. Takahashi, Y. Kawaguchi, H. Yamaguchi, A. Harada, *Macromolecules* 2005, *38*, 5897–5904; (c) J. Wang, M. Jiang, *J. Am. Chem. Soc.* 2006, *128*, 3703–3708; (d) M. Paolino, F. Ennen, S. Lamponi, M. Cernescu, B. Voit, A. Cappelli, D. Appelhans, H. Komber, *Macromolecules* 2013, *46*, 3215–3227; (e) H.-T. Nguyen, D.-T. Pham, S. F. Lincoln, J. Wang, X.-H. Guo, C. J. Easton, R. K. Prud'homme, *Polym. Chem.* 2013, *4*, 820–829.

13 W. Schnabel, Polymer Degradation: Principles and Practical Applications; Hanser: Munich, **1982**.

14 (a) Q. Lou, M. A. Kishpaugh, D. A. Shipp, *J. Polym. Sci., Part A: Polym. Sci.* **2010**, *48*, 943–951; (b) K.-M. Wang, R. Cui, J.-M. Gu, Q. Yu, G.-P. Ma, J. Nie, *J. Appl. Polym. Sci.* **2012**, *123*, 26–31.

15 (a) T. Kohara, *Macromol. Symp.* **1996**, *101*, 571–579; (b) L. L. Beecroft, C. K. Ober, *Chem. Mater.* **1997**, *9*, 1302–1317; (c) W. Caseri, *Macromol. Rapid Commun.* **2000**, *21*, 705–722; (d) G. Khanarian, H. Celanese, *Opt. Eng.* **2001**, *40*, 1024–1029; (e) G. Schottner, *Chem. Mater.* **2001**, *13*, 3422–3435; (f) K. Kuriki, Y. Koike, Y. Okamoto, *Chem. Rev.* **2002**, *102*, 2347–2356; (g) C. Lu, B. Yang, *J. Mater. Chem.* **2009**, *19*, 2884–2901; (h) M. G. Dhara, S. Banerjee, *Prog. Polym. Sci.* **2010**, *35*, 1022–1077; (i) A. Tagaya, Y. Koike, *Polym. J.* **2012**, *44*, 306–314.

16 (a) S. Yamago, *J. Polym. Sci., Part A: Polym. Chem.* 2006, 44, 1–12; (b) S. Yamago, *Chem. Rev.* 2009, *109*, 5051–5068; (c) S. Yamago, Y. Nakamura, In Polymer Science: A Comprehensive Reference; K. Matyjaszewski, M. Möller, Eds-in-Chief; G. W. Coates, M. Sawamoto, Vol. Eds.; Elsevier: Amsterdam, 2012, vol. 3, pp. 227–247; (d) S. Yamago, Y. Nakamura, *Polymer* 2013, *54*, 981–994.

17 (a) S. Yamago, K. Iida, J. Yoshida, *J. Am. Chem. Soc.* **2002**, *124*, 2874–2874; (b) S. Yamago, K. Iida, J. Yoshida, *J. Am. Chem. Soc.* **2002**, *124*, 13666–13667; (c) Y. Nakamura, Y. Kitada, Y. Kobayashi, B. Ray, S. Yamago, *Macromolecules* **2011**, *44*, 8388–8397; (d) Y. Nakamura, T. Arima, S. Tomita, S. Yamago, *J. Am. Chem. Soc.* **2012**, *134*, 5536–5539; (e) E. Mishima, T. Tamura, S. Yamago, *Macromolecules* **2012**, *45*, 8998–9003.

18 (a) A. Goto, Y. Kwak, T. Fukuda, S. Yamago, K. Iida, M. Nakajima, J. Yoshida, J. Am. Chem. Soc. 2003, 125, 8720–8721;
(b) Y. Sugihara, Y. Kagawa, S. Yamago, M. Okubo, Macromolecules 2007, 40, 9208–9211;
(c) S. Yusa, S. Yamago, M. Sugahara, S. Morikawa, T. Yamamoto, Y. Morishima, Macromolecules 2007, 40, 5907–5915;
(d) E. Kayahara, S. Yamago, Y. Kwak, A. Goto, T. Fukuda, Macromolecules 2008, 41, 527–529;
(e) M. Okubo, Y. Sugihara, Y. Kitayama, Y. Kagawa, H. Minami, Macromolecules 2009, 42, 1979–1984;
(f) S. Kumar, M. Changez, C. N. Murthy, S. Yamago, J.-S. Lee, Macromol. Rapid Commun. 2011, 32, 1576–1582;
(g) S. Feng, W. Xu, K. Nakanishi, S. Yamago, ACS Macro Lett. 2012, 1, 146–149;
(h) Y. Kitayama, K. Kishida, M. Okubo, J. Polym. Sci., Part A: Polym. Chem. 2013, 51, 716–723.

19 (a) K. Yamanishi, E. Sato, A. Matsumoto, *J. Photopolym. Sci. Technol.* **2013**, *26*, 239–244; (b) T. Inui, K. Yamanishi, E. Sato, A. Matsumoto, *Macromolecules* **2013**, *46*, 8111–8120.

20 N. Tanaka, E. Sato, A. Matsumoto, *Macromolecules* **2011**, *44*, 9125–9137.

21 T. Inui, E. Sato, A. Matsumoto, *ACS Appl. Mater. Interfaces* **2012**, *4*, 2124–2132.

22 A. Ozaki, K. Sumita, K. Goto, A. Matsumoto, *Macromolecules* 2013, *46*, 2941–2950.

23 A. Omayu, T. Ueno, A. Matsumoto, *Macromol. Chem. Phys.* **2008**, *209*, 1503–1514.

24 (a) F. Alvarez, J. Colmenero, C. H. Wang, J. L. Xia, G. Fytas, *Macromolecules* **1995**, *28*, 6488–6493; (b) M. Gaborieau, R. Graf, S. Kahle, T. Pakula, H. W. Spiess, *Macromolecules* **2007**, *40*, 6249–6256.

25 (a) T. Otsu, H. Watanabe, J.-Z. Yang, M. Yoshioka, A. Matsumoto, *Makromol. Chem., Macromol. Symp.* **1992**, *63*, 87–104; (b) A. Matsumoto, T. Otsu, *Macromol. Symp.* **1995**, *98*, 139–152.

26 M. Ouchi, N. Badi, J.-F. Lutz, M. Sawamoto, *Nat. Chem.* 2011, *3*, 917–924.