Control of Thermal, Mechanical, and Optical Properties of Three-Component Maleimide Copolymers By Steric Bulkiness and Hydrogen Bonding

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ABSTRACT: *N*-substituted maleimides polymerize in the presence of a radical initiator to give polymers with excellent thermal stabilities and transparency. In this study, we synthesized various maleimide copolymers with styrenes and acrylic monomers to control their thermal and mechanical properties by the introduction of bulky substituents and intermolecular hydrogen bonding. Three-component copolymers of *N*-(2-ethylhexyl)maleimide in combination with styrene, α -methylstyrene (MSt), or 1-methylenebenzocyclopentane (BC5) as the styrene derivatives, and *n*-butyl acrylate, 2-hydroxyethyl acrylate, 4-hydroxybutyl acrylate, or acrylic acid as the acrylic monomers were prepared by radical copolymerization. These copolymers were revealed to exhibit excellent heat resistance by

INTRODUCTION Thermoplastics are widely used because of the merits of easy processing with the application of heat and pressure as well as advantages for reuse and recycle, while thermosets readily exhibit excellent heat resistance and mechanical strength due to their network structures. It is expected to simultaneously have both features for thermoplastics and thermosets for forthcoming advanced polymer materials. Actually, the additions of certain thermal and mechanical properties are required depending on the case for the development of thermoplastic transparent polymer materials; for example, high glass transition (T_a) and decomposition temperatures, high mechanical strength and toughness, and optical properties such as high transparency and unique birefringence.¹⁻²³ N-substituted maleimides copolymerize with various kinds of vinyl monomers in the presence of a radical initiator to give copolymers with excellent thermal stabilities.^{24–26} The copolymerization of the maleimides with isobutene provided an alternating copolymer with an excellent thermal stability, transparency, and mechanical properties.²⁷⁻²⁹ AAB-type sequence-controlled polymers were also produced during the copolymerization of the Nsubstituted maleimides with diisobutene,³⁰⁻³² limonene,^{32,33} β -pinene,³⁴ and other sterically hindered olefins^{35,36} under penultimate unit control. The AAB-type copolymers exhibited a high T_a value due to a high content of the maleimide unit. The

thermogravimetric analysis. Glass transition temperatures increased by the introduction of bulky MSt and BC5 repeating units. The mechanical properties of the copolymer films were improved by the introduction of intermolecular hydrogen bonding. Optical properties, such as transmittance, refractive index, Abbe number, and birefringence, were determined for the copolymers. © 2019 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2019**

KEYWORDS: birefringence; glass transition temperature; hydrogen bond; maleimide; mechanical property; polymer film; radical polymerization; steric hindrance; thermal property; thermogravimetric analaysis (TGA); thin films; transparent polymer

copolymerization of the N-substituted maleimides with styrene (St) derivatives, such as α -methylstyrene (MSt) and 1-methylenebenzocycloalkanes, provided thermally stable polymers with high T_{a} but they were brittle to be provided for mechanical tests.^{30,37,38} The brittleness of the maleimide copolymers often becomes an obstacle for actual processing and applications. It is also noteworthy that the maleimide copolymers including an allyl group in the side chain were conveniently fabricated during the copolymerization of *N*-allylmaleimide with olefins.³⁹ The allylcontaining copolymers are useful as the precursor polymers for the synthesis of heat-resistant network polymers by a thiol-ene reaction in the presence of multifunctional crosslinkers,⁴⁰ but network structure formation is disadvantageous for the fabrication of transparent polymer films. The formation of a pseudonetwork structure using intermolecular hydrogen bonding may be effective for the maintenance of the desired thermal resistance and mechanical properties of transparent polymer films as well as the excellent processability.41-43

In this study, we designed the maleimide copolymers by the introduction of bulky and cyclic structures into the repeating units and intermolecular hydrogen bonding in the polymer side chains in order to control the thermal and mechanical

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properties of the copolymers. We prepared various copolymers using N-(2-ethylhexyl)maleimide (EHMI), a styrene monomer (RS), such as St, MSt, and 1-methylenebenzocyclopentane (BC5), and an acrylic monomer (RA), such as n-butyl acrylate (BA), 2-hydroxyethyl acrylate (HEA), 4-hydroxybutyl acrylate (HBA), and *tert*-butyl acrylate (tBA), as shown in Figure 1. The tBA repeating unit in the copolymers was transformed to an acrylic acid (AA) unit by heating in the presence of an acid. The thermal and mechanical properties as well as the optical properties of the cast films of the copolymers were investigated.

EXPERIMENTAL

General Procedures

The nuclear magnetic resonance (NMR) spectra were recorded in deuterated chloroform (CDCl₃) using JEOL ECS-400 and ECX-400 spectrometers. The infrared (IR) and ultraviolet-visible (UV-vis) spectra were recorded using JASCO FTIR-4600 and Shimadzu UV-2600 spectrometers, respectively. Size exclusion chromatography was carried out using Chromato Science CS-300C, JASCO PU-2080PLUS, JASCO DG-2080-53, JASCO RI-2031-PLUS, TOSOH TSK-gel columns, GMH_{HR}-N and GMH_{HR}-H, and tetrahydrofuran (THF) as the eluent. Number- and weight-average molecular weights ($M_{\rm p}$ and $M_{\rm w}$ respectively) and polydispersity ($M_{\rm w}/M_{\rm p}$) values were determined by calibration with standard polystyrenes. The thermogravimetric (TG) analysis was carried out in a nitrogen stream at the heating rate of 10 °C min⁻¹ using a Shimadzu DTG-60. The onset temperature of decomposition (T_{d5}) was determined as the 5% weight-loss temperature in the TG curves. The maximum temperature of the decomposition (T_{max}) was determined as the peak temperature of the differential TG curves. Differential scanning calorimetry (DSC) was carried out using a Shimadzu DSC-60 at the heating rate of 10 °C min⁻¹. The T_q values were determined from the curves observed during a second heating process. The tensile test was carried out using a Shimadzu Autograph AGS-X (10 kN cell load) at the tensile rate of 0.5 mm min⁻¹. Polymer films were prepared by casting the chloroform solution of a polymer



FIGURE 1 Monomers used for the synthesis of copolymers.

(5 wt %) and dried under atmospheric conditions for 24 h, then further dried *in vacuo* for 1 h with an oven at a desired temperature. Elasticity (Young modulus) was determined from the initial slope of the stress–strain curves (within 5% strain). The number of test pieces (50.0 mm width \times 9.0–12.0 mm length \times 120–340 µm thickness) was 2–10 for each measurement. The film thickness was measured using a thickness gauge (Peacock, 0.01 mm dial type, Ozaki MFG. Co., Ltd., Tokyo, Japan).

Optical Properties

The refractive indices ($n_{\rm F}$, $n_{\rm E}$, $n_{\rm D}$, and $n_{\rm C}$) were measured at the wavelengths of 486, 546, 589, and 656 nm, respectively, using an Abbe-type refractometer (Atago DRM2, 1-bromonaphthalene, a halogen lamp). The Abbe number ($\nu_{\rm D}$) was calculated as follows.

$$\nu_{\rm D} = (n_{\rm D} - 1) / (n_{\rm F} - n_{\rm C}) \tag{1}$$

The calculated refractive index values were fitted with the experimental results using the Cauchy equation (eq 2) as the two-parameter (n_{∞} and A) analysis method.⁴⁴

$$n_{\lambda} = n_{\infty} + A/\lambda^2 \tag{2}$$

where λ is the wavelength, n_{∞} is the refractive index at the infinite wavelength, n_{λ} is the refractive index at the wavelength of λ , and *A* is the constant.

The birefringence property of the selected copolymer films was evaluated according to the method reported in the literature^{9,45} at Material Solutions Research Institute, Kaneka Co. (Settsu, Japan). The cast films were stretched at a rate of 2.5 mm s⁻¹ and a determined temperature to fabricate test pieces used for orientational birefringence evaluation. Photoelastic birefringence was determined at 23 °C and 586.4 nm using a cast film of a copolymer consisting of EHMI, St, and HEA (**3a**), according to eq 3.

$$\Delta n = C\sigma \tag{3}$$

where C and σ are the photoelastic constant and the stress, respectively.

Materials

Maleic anhydride (MAn), 2-ethylhexylamine, acetic acid, sodium acetate, 1-indanone, methyltriphenylphosphonium bromide, and potassium *tert*-butoxide were purchased from Tokyo Chemical Industry, Co., Ltd. (Tokyo, Japan) and used as received. 2,2'-Azobisisobutyronitrile (AIBN) was purchased from Fujifilm Wako Pure Chemical Co. (Tokyo, Japan) and used after recrystallization from methanol. St and vinyl acetate (VAc) were purchased from Fujifilm Wako Pure Chemical Co., and MS, BA, HEA, HBA, and tBA were from Tokyo Chemical Industry, Co., Ltd. They were used after distillation. The solvents were purchased from Nacalai Tesque (Kyoto, Japan) and used after distillation. EHMI and BC5 were synthesized according to the methods reported in the literature.^{30,46}

N-(2-Ethylhexyl)maleimide

To 14.8 g (0.15 mol) of MAn dissolved in 150 mL of diethyl ether, 19.4 g (0.15 mol) of 2-ethylhexylamine in 50 mL of diethyl ether was slowly added at 0 °C, then the mixture was further stirred at room temperature for 1.5 h. After the reaction mixture was kept at -40 °C for 1 h, the precipitated *N*-(2-ethylhexyl)maleamic acid was isolated by filtration. The yield was 31.1 g. A mixture of the maleamic acid (31.1 g, 0.14 mol), acetic anhydride (140 mL), and sodium acetate (7.03 g) was stirred at 100 °C for 1 h. After the mixture was cooled to 0 °C, 180 mL of distilled water was added, then further stirred at room temperature for 2 h. The product was extracted with 120 mL of diethyl ether, washed with saturated aqueous NaHCO₃ and saturated aqueous NaCl, and then dried over anhydrous sodium sulfate. Silica gel column chromatography with *n*-hexane and ethyl acetate (8/2 in volume) provided 8.70 g of EHMI.

N-(2-Ethylhexyl)maleamic Acid

Colorless solid, yield 90%, ¹H NMR (400 MHz, CDCl₃): $\delta = 6.29$ (d, J = 12.9 Hz, CHCOOH, 1H), 6.20 (d, J = 12.9 Hz, CHCONH, 1H), 3.24–3.28 (m, NHCH₂, 2H), 1.45–1.49 (m, CH, 1H), 1.22–1.32 (m, CH₂, 8H), and 0.81–0.86 (m, CH₃, 6H).

N-(2-Ethylhexyl)maleimide

Colorless oil, yield 30%, ¹H NMR (400 MHz, CDCl₃): $\delta = 6.68$ (s, CH=, 2H), 3.41 (d, *J* = 7.7 Hz, NCH₂, 2H), 1.70–1.73 (m, CH, 1H), 1.22–1.28 (m, CH₂, 8H), and 0.8–1.0 (t, *J* = 7.1 Hz, CH₃, 6H).

1-Methylenebenzocyclopentane

A 1000 mL four-necked flask was charged with methyltriphenylphosphonium bromide (35.7 g, 100 mmol) suspended in dry THF (200 mL) under nitrogen. Potassium *tert*-butoxide

TABLE 1 Radical Copolymerization of RS, EHMI, and RA at 60 °C

(11.2 g, 100 mmol) was added, then the yellow mixture was stirred at 0 °C for 30 min. 1-Indanone (13.0 g, 100 mmol) was added dropwise, then the mixture was stirred for 16 h after being warmed to room temperature. A total volume of 150 mL of water was added to quench the excess reagent, and the product was extracted with diethyl ether (50 mL, six times). After dried on anhydrous sodium sulfate, the silica gel column chromatography with *n*hexane/ethyl acetate (9/1 in volume) as the eluent provided BC5. It should be careful to the undesirable isomerization of BC5 to 3-methylindene during the preparation and purification processes of BC5. The isomerization of BC5 and other exomethylene compounds, such as itaconic derivatives, in the presence of a basic compound was reported in the literature.^{47,48} In this study, acetone- d_6 was used for monitoring the reaction. The chemical structure of BC5 was checked again by 1 H NMR spectroscopy using CDCl₃ after purification and isolation.

Colorless oil, yield 17%,¹H NMR(400 MHz, CDCl₃): δ = 7.48–7.51 (m, C₆H₄, 1H), 7.18–7.28 (m, C₆H₄, 3H), 5.45 (t, *J* = 2.5 Hz, =CH₂, 1H), 5.03 (t, *J* = 2.5 Hz, =CH₂, 1H), 2.97–3.00 (m, CH₂C₆H₄, 2H), and 2.78–2.82 (m, =CCH₂, 2H).

Polymerization

The mixture of EHMI, RS, RA, or other monomers, AIBN, and chloroform or methyl ethyl ketone (MEK) were cooled with liquid nitrogen, degassed for 10 min at the same temperature, then the mixture was kept in a water bath for 20 min. These freeze-thaw cycles were repeated three times. The mixture was heated at 60 °C, and then the reaction mixture was poured into a large amount of methanol. The precipitated copolymer was filtered out, washed, and then dried *in vacuo* at room temperature. The yield of copolymers was gravimetrically determined. The copolymers

Copolymer	RS	RA	RS/EHMI/RA in Feed (mmol)	AIBN ^a (mol %)	CHCl ₂ (a)	Time (h)	Yield (%)	RS/EHMI/RA in Copolymer (mol %)	<i>M</i> × 10 ⁻⁴	<i>M/M</i> .,
1a	St	None	5 0/5 0/0	2.5	b	5	69	50/50/0	72	2.0
16 16	MSt	None	10 0/10 0/0	1.0	0	5	65	50/50/0	14.4	2.0
10	BC5	None	10.0/10.0/0	1.0	0	5	47	52/48/0	21.7	17
2a	St	BA	8.0/8.0/8.0	1.7	c	10	72	48/36/16	8.3	2.5
2h	MSt	BA	10 0/10 0/10 0	0.67	0	10	54	48/37/15	10.0	1.9
20	BC5	BA	4 0/4 0/5 3	1.0	0	10	35	45/40/15	11.7	2.4
20 3a	St	HFA	7.5/7.6/7.6	1.0	5 7.6	2	51	44/38/18	32.3	1.8
3b	MSt	HFA	10 0/10 0/10 0	0.67	8.3	-	46	51/41/8	16.2	1.9
3c	BC5	HFA	8.0/8.0/8.0	0.67	0	10	19	49/40/11	10.2	1.8
4a	St	HBA	7.5/7.0/9.0	1.9	10.7	2	45	43/39/18	26.3	1.7
4b	MSt	HBA	8.0/8.0/8.0	0.75	1.6	4	48	46/38/16	14.9	1.9
4b′	MSt	HBA	8.0/8.0/16.0	0.75	2.1	4	41	46/36/18	16.9	1.8
4b″	MSt	HBA	8.0/4.0/16.0	1.0	1.8	4	19	46/35/19	9.7	1.6
4c	BC5	HBA	8.5/9.1/10.0	0.72	0	7.5	35	43/46/11	12.7	2.0
5a	St	tBA	8.0/8.0/8.0	0.83	8.3	2	57	45/41/14	28.0	2.0
5b	MSt	tBA	8.0/8.0/8.0	0.75	1.6	- 8	46	44/48/8	12.4	1.8
5c	BC5	tBA	7.3/7.3/7.3	1.0	0	10	64	46/48/6	15.7	1.8

^aBased on the total amount of monomers. ^b[EHMI] = [St] = 0.40 mol L⁻¹. c [EHMI] = [St] = [BA] = 0.40 mol L⁻¹.





FIGURE 2 Repeating structure of copolymers synthesized in this study.

were purified by repeated precipitation procedures using chloroform and methanol, then the copolymer composition was determined by ¹H NMR spectroscopy. For the determination of the tBA content, the weight loss observed during TG measurement was also available (see typical TG curves in Fig. S4 of Supporting Information).

RESULTS AND DISCUSSION

Synthesis of Copolymers

The maleimide copolymers consisting of EHMI and the RSs (St, MSt, and BC5) were prepared in the absence of the RAs (**1a-1c**) and in the presence the RAs (**2a-2c** for BA, **3a-3c** for HEA, **4a-4c** for HBA, and **5a-5c** for tBA) by radical copolymerization with AIBN in chloroform or in bulk at 60 °C. The

results of copolymerization are summarized in Table 1. Figure 2 shows the repeating unit structures of the copolymers obtained in this study.

The alternating copolymers of EHMI and the RSs (**1a-1c**) with a high molecular weight ($M_w = 7.2-21.7 \times 10^4$) were readily produced in a high yield (47–69%), being in good agreement with the results reported in the literature.^{24–26,37} The further addition of BA to the copolymerization systems of EHMI and the RSs provided the corresponding three-component copolymers (**2a–2c**). The contents of BA in the copolymers were always lower than those in the feed. This was because the cross-propagation between EHMI and the RSs was preferred rather than the propagation of BA. It was reported that acrylate and maleimide monomers exhibited similar monomer



SCHEME 1 Transformation of the tBA-containing copolymers (5a-5c) to the AA-containing copolymers (6a-6c).

TABLE 2 Radical Copolymerization of RS (M_1) and Various Monomers (M_2) at 60 °C

		RS/M_2 in	AIBN ^a				RS/M ₂ in		
M ₁ (RS)	M_2	Feed (mmol)	(mol %)	Solvent (mL)	Time (h)	Yield (%)	Copolymer (mol %)	$M_{\rm w} imes 10^{-4}$	$M_{\rm w}/M_{\rm n}$
BC5	BA	5.0/5.0	1.0	None	10	3	63/37	1.0	1.5
BC5	St	5.0/5.1	1.0	None	10	1	76/24	0.5	1.8
BC5	VAc	5.0/5.0	1.0	None	10	Trace	b	b	b
BC5	EHMI	10.0/10.0	1.0	None	5	47	52/48	22	1.7
BC5	MAn	1.8/1.8	0.56	MEK ^c (0.5)	10	30	47/53	3.4	2.2
MSt	BA	21.0/9.0	1.0	None	17	35	44/56	3.6	1.7
MSt	MAn	14.0/14.0	1.1	MEK ^c (4.0)	4	50	50/50	10.6	1.7
St	BA	21.0/9.0	1.0	None	11	82	32/68	25	2.0
St	MAn	14.8/14.8	1.0	MEK ^c (15.0)	10	83	b	24.4	4.4

^aBased on the total amount of monomers. ^bNot determined. ^cMEK, methyl ethyl ketone.

reactivity ratios during the mutual copolymerization systems; for example, monomer reactivity ratios were $r_1 = 0.71$ and $r_2 = 0.77$ for the copolymerization of methyl acrylate (M₁) and *N*-cyclohexylmaleimide (M₂).²⁵ It is speculated that the copolymers produced in the present three-component copolymerization mainly consist of an alternating structure of EHMI and RS units, of which the EHMI repeating unit was partly substituted by BA.

Similarly, HEA, HBA, and tBA were incorporated into the copolymers of EHMI and the RSs. Here, the tBA was used for the preparation of the precursor copolymers for those containing an AA repeating unit. The AA-containing copolymers (**6a–6c**) were prepared by heating of the corresponding tBA-containing copolymers (**5a–5c**) in the presence of *p*-toluenesulfonic acid in toluene at 110 °C for 5 h (Scheme 1).¹³

TABLE 3 Thermal and Mechanical Properties of the Copolymers Synthesized in this Study

	Thermal	Properties		Mechanical Properties				
Copolymer	<i>T_g</i> (°C)	<i>Т</i> _{d5} (°С)	T _{max} (°C)	Number of Samples	Young Modulus (MPa)	Maximum Strength (MPa)	Strain at Break (%)	
1a	90	351	431	а	а	а	а	
1b	116	317	378	а	а	а	а	
1c	109	330	377	а	а	а	а	
2a	53	298	424	3	$\textbf{224} \pm \textbf{38}$	$\textbf{1.86} \pm \textbf{1.13}$	$\textbf{1.49} \pm \textbf{0.72}$	
2b	77	314	380	а	а	а	а	
2c	92	320	384	а	а	а	а	
3a	78	328	434	10	$\textbf{707} \pm \textbf{65}$	$\textbf{13.7} \pm \textbf{1.54}$	$\textbf{3.38} \pm \textbf{0.95}$	
3b	103	294	387	5	674 ± 73	$\textbf{3.97} \pm \textbf{2.42}$	$\textbf{0.75} \pm \textbf{0.48}$	
3c	104	311	388	5	531 ± 109	$\textbf{0.95} \pm \textbf{0.32}$	$\textbf{0.24} \pm \textbf{0.07}$	
4a	73	358	426	3	620 ± 92	10.02 ± 1.71	$\textbf{2.61} \pm \textbf{0.70}$	
4b	93	322	388	5	662 ± 47	$\textbf{3.68} \pm \textbf{0.72}$	$\textbf{0.66} \pm \textbf{0.15}$	
4b′	91	342	392	_	_	-	_	
4b″	87	339	388	-	-	-	-	
4c	97	319	389	10	$\textbf{766} \pm \textbf{92}$	$\textbf{3.47} \pm \textbf{1.30}$	$\textbf{0.53} \pm \textbf{0.20}$	
5a	86	258 ^b	257 ^b , 435	-	-	-	-	
5b	106	303 ^b	269 ^b , 388	-	-	-	-	
5c	97	265 ^b	245 ^b , 375	-	-	-	-	
6a	102	366	427	3	641 ± 30	$\textbf{7.72} \pm \textbf{2.13}$	$\textbf{1.93} \pm \textbf{0.70}$	
6b	126	339	390	2	694 ± 18	$\textbf{2.71} \pm \textbf{0.15}$	$\textbf{0.47} \pm \textbf{0.05}$	
6c	120	297	381	2	$\textbf{793} \pm \textbf{23}$	$\textbf{2.58} \pm \textbf{0.39}$	$\textbf{0.37} \pm \textbf{0.05}$	
7b	233	308	342	4	1385 ± 171	$\textbf{2.18} \pm \textbf{0.13}$	$\textbf{0.21} \pm \textbf{0.04}$	
8b	70	296	341	а	а	а	а	

^aToo brittle to be measured.

ADVANCED SCIENCE NEWS ^bFor the elimination of isobutene from the *tert*-butyl ester in the side chain.



FIGURE 3 TG curves of (a) **4a** (dash), **4b** (dot), and **4c** (solid) and (b) **5c** (solid) and **6c** (dash) in nitrogen stream at the heating rate of 10 $^{\circ}$ C min⁻¹.

The RS contents were almost constant in a range of 43-52 mol % for the all copolymerization systems. The RA contents varied in 6-19 mol % gently depending on the RSs, that is, the RA content slightly decreased according to the substituent in the RS unit as follows; St > MSt > BC5. The apparent copolymerization rate and the molecular weight of the copolymers showed similar tendency, but more detailed discussion for the relative reactivity in this system was difficult because we have no data under unified copolymerization conditions. Recently, the acceleration of the propagation rate of vinyl monomers containing a hydroxy group was reported for several polymerization systems, in which intermolecular and intramolecular hydrogen bonding is important to extraordinary enhancement of monomer reactivity.⁴⁹⁻⁵¹ Being different from the results reported in the literature, no outstanding incorporation of HEA and BHA was confirmed in this study because of fast cross-propagations between EHMI and RS. When the copolymerization was carried out using various comonomer ratios in the feed, that is, [RS]/[EHMI]/[HBA] = 1/1/1, 1/1/2,and 1/0.5/2 in molar ratio for the preparation of the copolymers **4b**, **4b**', and **4b**'', respectively, the copolymer composition slightly varied (see Table 1). The control of the RA content was difficult by a change in the comonomer feed under the copolymerization conditions used in the present study. Consequently, we used the three-component copolymers containing the RA units in a limited range of 6–19 mol %, as shown in Table 1.

In contrast to the production of the high molecular weight copolymers from BC5 during the copolymerization in the



FIGURE 4 Effect of the structure of the RSs and the RAs on the T_g values of the copolymers with EHMI. See Table 1 for the copolymer compositions. [Color figure can be viewed at wileyonlinelibrary.com]

presence of EHMI, the copolymers with a low molecular weight ($M_w < 10^4$) were produced in a low yield (less than 3%) during copolymerization of BC5 with BA, St, and Vac in the absence of EHMI, as shown in Table 2. The two-component copolymerization of BC5 combined with EHMI provided a high molecular weight and alternating copolymer in a high yield, as was expected.³⁰ The copolymerization of MSt or St with BA produced random copolymers. The BA content in the copolymers increased in the following order: St (68 mol % for BA unit) > MSt (56 mol % for BA unit) > BC5 (37 mol % for BA unit). These random copolymers with BA were of high molecular weight, but it was difficult to provide tough films.

Thermal Property

Table 3 summarizes the thermal properties of the copolymers synthesized in this study. The T_g values were determined by DSC and the T_{d5} and T_{max} values were determined by TG analysis at the heating rate of 10 °C min⁻¹ in a nitrogen stream.

Typical TG curves are shown in Figure 3. The copolymers containing a *tert*-butyl ester (**5a**–**5c**) showed the T_{d5} and T_{max} values lower than those for the other copolymers because the elimination of isobutene from the ester alkyl group quantitatively occurred upon heating.52-54 In fact, the weight loss started at approximately 250 °C and the $T_{\rm max}$ values were 245–269 °C. The copolymers isolated after heating were confirmed to have the repeating unit structure, of which the tBA repeating units were transformed to the AA repeating units (6a-6c) by NMR and IR spectroscopies (Scheme 1). For the copolymers other than **5a–5c**, the T_{d5} values were 294–358 °C and the T_{max} values were 377-434 °C, being much higher than decomposition temperatures for conventional vinyl polymers. The copolymers with MSt and BC5 exhibited lower T_{d5} and T_{max} values compared with those for the copolymers with St. This was due to the occurrence of depolymerization during the thermal decomposition of copolymers containing 1,1-disubstituted ethylene monomer units.

In the DSC traces for the copolymers, the glass transition was clearly observed, as shown in Figure S6. No peak due to a

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FIGURE 5 Stress-strain curves for the tensile test of various three-component maleimide copolymer films. (a) 2a (solid), 3a (dash), 4a (dot), (b) 3a (solid), 3b (dash), 3c (dot), (c) 4a (solid), 4b (dash), 4c (dot), and (d) 3c (solid), 4c (dash), and 6c (dot).

crystalline polymer indicates that the copolymers synthesized in this study are amorphous. The T_g values for the two-component copolymers were 90–116 °C (**1a–1c**). The copolymers with MSt and BC5 including the bulky substituents exhibited the higher T_g values. While the introduction of BA into the copolymers decreased the T_g values ($T_g = 53-92$ °C for **2a–2c**), the presence of a hydroxy group kept the T_g values in the range of 73–97 °C for **4a–4c** and the shorter alkyl spacer further increased ($T_g = 78-104$ °C for **3a–3c**), as shown in Figure 4. The copolymers containing AA (**6a–6c**) showed the highest T_g values. This indicates the significant contribution of intermolecular interaction via strong hydrogen bonding between the carboxylic acids.^{28,43} For the all cases, it was revealed that the introduction of the bulky MSt and BC5 units and the hydrogen bonding were valid for an increase in T_g of the copolymers.

Mechanical Property

Table 3 also summarized the results of the mechanical properties evaluated by the tensile test of the copolymer films. The films with a thickness of $120-340 \ \mu m$ were prepared by a casting method using chloroform as the solvent. Transparent and tough films were obtained from the copolymers including the RA units with hydroxy and carboxylic acid groups. In contrast, two-component copolymers and the three-component copolymers including no polar

substituent gave only brittle films. The film of 2a was provided for the tensile test, but a maximum strength, a strain at break, and Young modulus were much low as 1.86 MPa, 1.5%, and 224 MPa, respectively. Being different from the result of 2a, the copolymers of St and EHMI with various RAs including polar substituents exhibited maximum strength values in a range of 7.7-13.7 MPa and strain at break of 1.9-3.4% [Fig. 5(a)]. The Young moduli also increased to 531-766 MPa by the combination with HEA. HBA. and AA. Unfortunately, the introduction of bulky MSt and BC5 units decreased in the toughness of the films, that is, both the maximum strength and strain at break decreased as shown in Figure 5(b,c). The main chain mobility might be reduced by the introduction of 1,1-disubstituted ethylene units, such as MSt and BC5, leading to an increase in the T_q of the copolymers and simultaneously a decrease in the mechanical strength. The toughness of the copolymers depended on the ester alkyl groups of the RA unit. The maximum strength and strain values decreased in the following order: **4c** > **6c** > **3c**, as shown in Figure 5(d).

As already described, the two-component copolymers of EHMI with the RSs including no hydroxy and carboxylic acid groups are too brittle to be used as the polymer films for the measurement of mechanical properties. One of the reasons for the poor mechanical property is the presence of ring structure in



SCHEME 2 Synthesis of the alternating copolymer of MAn and MSt (**7b**) and transformation to the diester copolymer (**8b**) by the reaction of **7b** with *n*-butanol in MEK by reflux for 3.5 h in the presence of an acid catalyst. $R'' = (CH_2)_3 CH_3$.





FIGURE 6 (a) IR and (b) ¹H NMR spectra of **7b** and **8b** (after transformation of **7b** to the diester copolymer). Asterisk indicates peaks due to water and solvents. [Color figure can be viewed at wileyonlinelibrary.com]

the polymer main chain. It has been reported that the homopolymers of *N*-substituted maleimides have outstanding heat resistance, but too brittle and fragile to be used for various applications.⁵⁵ In addition, the homopolymerization reactivity of the *N*-substituted maleimides is not so high due to their sterically hindered 1,2-disubstituted ethylene monomer structure. In the most cases, therefore, they were used as the copolymers with conventional vinyl monomers. The maleimide copolymers

TABLE 4 Optical Properties of the Maleimide Copolymer Films

Copolymer	Transmittance at 380 nm (%)	<i>n</i> _D (589 nm)	$\nu_{\rm D}{}^{\rm a}$
1a	96.7	1.533	41.8
2a	97.9	1.533	38.6
3a	97.3	1.523	41.5
4a	96.7	1.524	42.2
6a	94.5	1.530	43.1
1c ^b	94.8	1.543	42.9
2c	96.3	1.548	45.3
3c	97.0	1.550	40.7
4c	93.9	1.538	42.3
6c	91.9	1.543	37.0

^aAbbe number: $\nu_D = (n_D-1)/(n_F-n_C)$. ^bCited from Ref. 30.

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can be derived from the copolymers of MAn with the corresponding comonomers by the polymer reactions consisting of ring opening with an amine and the subsequent maleimide-ring formation by dehydration upon heating.⁵⁶ According to a similar procedure, the diester copolymers would be readily produced.^{57,58} In the present study, we synthesized the alternating copolymer (**8b**) of MSt and di-*n*-butyl maleate by the reaction of the alternating copolymer of MSt and MAn (**7b**) with *n*-butanol in MEK by reflux (Scheme 2).

As shown in Table 2, the copolymerization of MAn with St and MSt produced high molecular weight polymers ($M_{\rm w} = 10.6 - 24.4 \times 10^4$) in high yield (50-83%). Being different from them, the copolymer with BC5 with a lower M_w was obtained in a lower yield. The ringopening reaction of the alternating copolymer of MAn with MSt (7b) was monitored by IR spectroscopy. From comparison of the IR spectra of 7b before and after the reaction [Fig. 6(a)], an intensity of peaks characteristic to an anhydride group (the symmetric and asymmetric stretching vibrations of a C=O bond at 1858 and 1780 cm⁻¹, respectively) decreased and the peaks due to the ester group newly appeared at 1735 cm^{-1} (C=O stretching vibration) and 1170 cm⁻¹ (C(=0)-0 stretching vibration). In ¹H NMR spectrum of the product [Fig. 6(b)], peaks assigned as the *n*-butyl ester groups were detected. It was concluded based on the intensity ratio of the characteristic peaks that the transformation quantitatively proceeded. When the mechanical properties of **7b** were evaluated, it was revealed to a high Young modulus (1385 MPa) and low strength and strain values at break (2.18 MPa and 0.21%,



FIGURE 7 (a) Transmittance of the copolymer films in UV-vis region of **4c** (solid) and **1c** (dash). (b) Wavelength dependence of refractive indices for **4a**, **4c**, **6a**, and **6c**.

Polymer	Intrinsic Birefringence nº (×10 ⁻³)	Photoelastic Coefficient $C (\times 10^{-12}, Pa^{-1})$	Ref.
3a	-	0.7	This study
Polystyrene	-110	8.8	59,60
Poly(MSt)	-91	-3.7	60,61
Poly(<i>N</i> -methylmaleimide)	53.8	11.9	10
Poly(methyl methacrylate)	-5.6, -6.1	-5.5, -4.3	4,45
Poly(benzyl methacrylate)	19.5	48.4	4
Poly(cyclohexyl methacrylate)	-2.3	6.21	45

TABLE 5 Birefringence Properties of 3a and Other Polymers

respectively). The T_g of **7b** was much high as 233 °C and the decomposition temperature were also high ($T_{d5} = 308$ °C and $T_{max} = 342$ °C). Thus, it was confirmed that the copolymer containing an anhydride ring structure in the main chain was thermally stable but too hard and brittle for the use as tough film materials. The esterification of the copolymer resulted in a drastic decrease in the T_g value while the decomposition temperatures were the same. The produced diester copolymer **8b** was too brittle to be evaluated by a tensile test, as shown in Table 3.

Optical Property

In Table 4, transmittance at 380 nm, reflective index (D line, 589 nm), and Abbe number [$\nu_{\rm D} = (n_{\rm D}-1)/(n_{\rm F}-n_{\rm C})$] for each copolymer are shown. All the copolymer films showed excellent transmittance [Fig. 7(a)] except for **6c** with transmittance of 91.9%. The copolymers containing the carboxylic acid group, that is, **6a** and **6c**, exhibited transmittance values lower than those for the copolymers with St (**1a-4a**) and BC5 (**1c-4c**), respectively. The reflective indices were 1.524–1.533 and 1.543–1.550 for the copolymers with St and BC5, respectively. The latter exhibited higher $\nu_{\rm D}$ values because of a decrease in the RA unit in the copolymers, resulting in an increase in the relative contents of EHMI [Fig. 7(b)]. The observed Abbe numbers (37.0–45.3) were closed to the values reported for the other maleimide copolymers in the literature.^{14,26}



FIGURE 8 Orientational birefringence of 3a (solid) and 6a (dash). The films of 3a and 6a were drawn at 100 and 113 °C, respectively.

In Table 5, the results for the evaluation of the birefringence properties of the copolymers are shown. The orientational birefringence was evaluated for the copolymer films stretched at different drawing ratios (Fig. 8). In this study, intrinsic birefringence values were not determined because the degree of orientation was unknown. As a result, 3a and 6a had small and minus birefringence values. It has been reported that polystyrene and poly(MSt) show a large intrinsic birefringence with a minus $sign^{59-61}$ while poly(Nmethylmaleimide) shows a plus intrinsic birefringence.¹⁰ Poly(alkyl methacrylate)s including poly(methyl methacrylate) have a small intrinsic birefringence.4,45 The threecomponent copolymers produced in this study consist of the styrene, maleimide, and acrylate units as the repeating structures. The EHMI and the RSs units are expected to exhibit birefringence properties similar to those for poly(Nmethylmaleimide) and poly(alkyl methacrylate)s, respectively. Based on the copolymer compositions of 3a and 5a, a small and minus birefringence was considered to be of a result for the offset of polarization along the main chain by the maleimide ring included in the EHMI repeating unit and polarization orthogonal to the main chain by the benzene ring included in the St repeating unit.

In this study, the photoelastic coefficient of **3a** was successfully determined to be 0.7×10^{-12} Pa⁻¹. This value was one order smaller than those for other conventional and related polymers, for example, 8.8×10^{-12} Pa⁻¹ for polystyrene and -4.3 to -5.5×10^{-12} Pa⁻¹ for poly(methyl methacrylate). A photoelastic coefficient is the parameter which is closely related to the fashion of the segment mobility of poly(methyl methacrylate) comes from the reorientation of the side chain. The sign of the coefficients also significantly depends on the polymer structures. The unique birefringence properties of the maleimide copolymers will attract attention in the research fields of optical polymer materials and their applications. Further investigation on the birefringence of the maleimide copolymers is now continued.

CONCLUSIONS

In this study, we synthesized various three-component copolymers consisting of EHMI, styrenes, and acrylates containing a hydroxy or carboxylic acid group in the side chain and investigated their



thermal, mechanical, and optical properties. The T_q values increased by using MSt and BC5 instead St because of the restricted rotation of the main chain. All the copolymers exhibited high onset temperatures for decomposition. The mechanical properties were improved by the introduction of intermolecular hydrogen bonding although the introduction of a bulky styrene unit decreased the toughness of the films. For the simultaneous achievement of a high T_a and a high strength and strain at break, the presence of maleimide ring structure in the main chain and intermolecular interaction between polymer chains in addition to the balance of the steric bulkiness along the polymer main chain. The preliminary birefringence test in this study opened a new possibility of the maleimide copolymers for the application as the thermally stable and highly transparent polymer films with unique optical features.

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CONFLICT OF INTEREST

The authors declare no conflict of interest.

REFERENCES AND NOTES

1 S. Ando, T. Matsuura, S. Sasaki, *Macromolecules* 1992, *25*, 5858.

2 L. Martinu, D. Poitras, J. Vac. Sci. Technol. A 2000, 18, 2619.

3 H. Wang, P. Xu, W. Zhong, L. Shen, O. Du, *Polym. Degrad. Stab.* **2005**, *87*, 319.

4 A. Tagaya, H. Ohkita, T. Harada, K. Ishibashi, Y. Koike, *Macro-molecules* **2006**, *39*, 3019.

5 M.-C. Choi, Y. Kim, C.-S. Ha, Prog. Polym. Sci. 2008, 33, 581.

6 M. Nogi, H. Yano, Adv. Mater. 2008, 20, 1849.

7 D. Zhou, H. Teng, K. Koike, Y. Koike, Y. Okamoto, *J. Polym. Sci. Part A: Polym. Chem.* **2008**, *46*, 4748.

8 K. Koike, F. Mikes, Y. Okamoto, Y. Koike, *J. Polym. Sci. Part A: Polym. Chem.* 2009, 47, 3352.

9 S. Iwasaki, Z. Satoh, H. Shafiee, A. Tagaya, Y. Koike, *Polymer* **2012**, *53*, 3287.

10 S. Beppu, S. Iwasaki, H. Shafiee, A. Tagaya, Y. Koike, *J. Appl. Polym. Sci.* **2014**, *131*, 40423.

11 S. Beppu, H. Hotta, H. Shafiee, A. Tagaya, Y. Koike, *Appl. Opt.* **2015**, *54*, 779.

12 N. Tanaka, E. Sato, A. Matsumoto, *Macromolecules* 2011, 44, 9125.

13 Y. Nakano, E. Sato, A. Matsumoto, *J. Polym. Sci. Part A: Polym. Chem.* **2014**, *52*, 2899.

14 A. Matsumoto, ACS Symp. Ser. 2014, 1170, 301.

15 Y. Minami, K. Murata, S. Watase, A. Matsumoto, K. Matsukawa, *J. Photopolym. Sci. Technol.* **2013**, *26*, 491.

16 R. Oban, K. Matsukawa, A. Matsumoto, *J. Polym. Sci. Part A: Polym. Chem.* **2018**, *56*, 2294.

17 H.-J. Ni, J.-G. Liu, Z.-H. Wang, S.-Y. Yang, *J. Ind. Eng. Chem.* 2015, *28*, 16.

18 E. K. MacDonald, M. P. Shaver, *Polym. Int.* **2015**, *64*, 6.

19 T. Higashihara, M. Ueda, Macromolecules 2015, 48, 1915.

20 C.-L. Tsai, H.-J. Yen, G.-S. Liou, *React. Funct. Polym.* 2016, 108, 2.

21 R. Hihumi, I. Tomita, Macromolecules 2018, 51, 5594.

22 R. Hihumi, I. Tomita, Polym. J. 2018, 50, 467.

23 R. Hihumi, I. Tomita, *Polym. J.* in press. https://doi.org/10. 1038/s41428-019-0200-9.

24 A. Matsumoto, T. Kubota, T. Otsu, *Macromolecules* **1990**, *23*, 4508.

25 T. Otsu, A. Matsumoto, T. Kubota, Polym. Int. 1991, 25, 179.

26 A. Matsumoto, M. Hisano, D. Yamamoto, H. Yamamoto, H. Okamura, *Kobunshi Ronbunshu* **2015**, *72*, 243.

27 T. Doi, Y. Sugiura, S. Yukioka, A. Akimoto, *J. Appl. Polym. Sci.* 1996, *61*, 853.

28 A. Omayu, T. Ueno, A. Matsumoto, *Macromol. Chem. Phys.* 2008, 209, 1503.

29 A. Matsumoto, D. Yamamoto, *J. Polym. Sci. Part A: Polym. Chem.* **2016**, *54*, 3616.

30 M. Hisano, K. Takeda, T. Takashima, Z. Jin, A. Shiibashi, A. Matsumoto, *Macromolecules* **2013**, *46*, 3314.

31 M. Hisano, K. Takeda, T. Takashima, Z. Jin, A. Shiibashi, A. Matsumoto, *Macromolecules* **2013**, *46*, 7733.

32 S. Terada, A. Matsumoto, Polym. J. in press.

33 K. Satoh, M. Matsuda, K. Nagai, M. Kamigaito, *J. Am. Chem. Soc.* **2010**, *132*, 10003.

34 D. Yamamoto, A. Matsumoto, *Macromol. Chem. Phys.* **2012**, *213*, 2479.

35 M. Matsuda, K. Satoh, M. Kamigaito, *J. Polym. Sci. Part A: Polym. Chem.* **2013**, *51*, 1774.

36 M. Matsuda, K. Satoh, M. Kamigaito, *Macromolecules* 2013, 46, 5473.

37 M. Hisano, T. Takashima, Z. Jin, A. Shiibashi, A. Matsumoto, Macromol. Chem. Phys. 2013, 214, 1612.

38 K. Takeda, A. Matsumoto, *Macromol. Chem. Phys.* **2010**, *211*, 782.

39 K. Takeda, A. Omayu, A. Matsumoto, *Macromol. Chem. Phys.* **2013**, *214*, 2091.

40 R. Semba, R. Oban, A. Matsumoto, *J. Adhes. Soc. Jpn.* **2017**, *53*, 235.

41 R. F. M. Lange, M. van Gurp, E. W. Meijer, *J. Polym. Sci. Part A: Polym. Chem.* **1999**, *37*, 3657.

42 A. Omayu, A. Matsumoto, Polym. J. 2008, 40, 736.

43 A. Omayu, S. Yoshioka, A. Matsumoto, *Macromol. Chem. Phys.* **2009**, *210*, 1210.

44 F. A. Jenkins, H. F. White, *Fundamentals of Optics*, 4th ed.; McGraw-Hill: New York, **1976**, p. 479.

45 H. Shafiee, A. Tagaya, Y. Koike, *J. Polym. Sci. Part B: Polym. Phys.* **2010**, *48*, 2029.

46 K. Chino, T. Takata, T. Endo, Macromolecules 1995, 28, 5947.

47 H. Ohishi, Y. Kosaka, K. Kitazawa, R. Goseki, S. Kawauchi, T. Ishizone, *Macromolecules* **2015**, *48*, 6900.

48 A. Matsumoto, S. Umehara, H. Watanabe, T. Otsu, *J. Polym. Sci. Part B: Polym. Phys.* **1993**, *31*, 527.

49 S. Sugihara, Y. Kawamoto, Y. Maeda, *Macromolecules* **2016**, *49*, 1563.

50 J. E. S. Schier, D. Cohen-Sacal, R. A. Hutchinson, *Polym. Chem.* 2017, *8*, 1943.

51 M. Iseki, Y. Suzuki, H. Tachi, A. Matsumoto, *ACS Omega* **2018**, *3*, 16357.

52 D. H. Grant, N. Grassie, Polymer 1960, 1, 445.

53 T. Otsu, T. Yasuhara, K. Shiraishi, S. Mori, *Polym. Bull.* 1984, 42, 449.

54 T. Otsu, A. Tatsumi, A. Matsumoto, J. Polym. Sci. Part C: Polym. Lett. 1986, 24, 113.

55 T. Otsu, A. Matsumoto, T. Kubota, S. Mori, *Polym. Bull.* 1990, 23, 43.

56 K. Nomura, A. Tsujii, A. Matsumoto, *Macromol. Chem. Phys.* 2017, *218*, 1700156.

57 T. Otsu, A. Matsumoto, K. Nakamura, *J. Appl. Polym. Sci.* 1992, 45, 1889.

58 G. Moriceau, G. Gody, M. Hartlieb, J. Winn, H.-S. Kim, A. Mastrangelo, T. Smith, S. Perrier, *Polym. Chem.* **2017**, *8*, 4152.

59 T. Inoue, H. Okamoto, K. Osaki, *Macromolecules* 1991, *24*, 5670.

60 Y. Okada, O. Urakawa, T. Inoue, Polym. J. 2016, 48, 1073.

61 T. Inoue, E. J. Hwang, K. Osaki, J. Rheol. 1992, 36, 1737.

