Thermal Properties of *N*-Phenylmaleimide-Isobutene Alternating Copolymers Containing Polar Groups to Form Intermolecular and Intramolecular Hydrogen Bonding

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We have demonstrated that the alternating copolymers obtained from *N*-phenylmaleimides having hydroxy and carboxy substituents and isobutene show excellent thermal stabilities; namely, onset temperatures of decomposition higher than 350 °C and glass transition temperatures higher than 220 °C, depending on the structure and position of the polar groups in the *N*-phenyl group. The obtained copolymers were soluble in organic solvents, such as dimethyl sulfoxide, dimethylformamide, tetrahydrofuran, and acetone, and transparent and brittle films were obtained by casting from their acetone solutions. The role of intermolecular hydrogen bonding for an increase in the glass transition temperature by the introduction of the polar groups was investigated by temperature-controlled IR spectroscopy. The formation of intramolecular hydrogen bonding for the *N*-2-hydroxyphenyl derivative was also revealed. The molecular conformations were discussed on the basis of the results of DFT calculations for the model compounds of the repeating unit in the copolymers.
KEY WORDS: Radical Copolymerization / Alternating Copolymer / Thermal Stability / Glass Transition Temperature / DFT Calculations / Hydrogen Bonding / Infrared Spectroscopy /

Recently, new thermo-resistant polymers with a high transparency attract a great interest as key materials for optoelectronic applications. The radical polymerization and copolymerization of *N*-phenylmaleimide (PhMI, **1**) and the thermal properties of the resulting polymers have been extensively studied in order to obtain thermally stable vinyl polymers.[1–3] At the same time, various kinds of PhMI derivatives have also been synthesized and polymerized.[4–12] When alkyl substituents were introduced in the *N*-phenyl group, the polymers were soluble in non-polar solvents and showed an excellent thermal decomposition property, while poly(**1**) was soluble in limited kinds of polar solvents.[13,14] On the other hand, the introduction of polar substituents resulted in the formation of polymers with poor solubility. For example, thermally stable polymers were synthesized by the polymerization of *N*-(hydroxyphenyl)-, *N*-(carboxyphenyl)-, and *N*-(trifluoromethylphenyl)maleimides, but they were insoluble or had a very limited solubility in solvents.[4,15–17] In 1996, Doi and coworkers reported that the alternating copolymerization of *N*-alkylmaleimides (RMI) with isobutene (IB) [poly(RMI-*alt*-IB)] produces high molecular weight copolymers with excellent thermal properties, as well as excellent mechanical and optical properties.[18–21] Poly(RMI-*alt*-IB)s are soluble in a larger number of organic solvents and had a moderate softening temperature. The processing of poly-(RMI-*alt*-IB)s can be easily carried out for the fabrication of polymer films, sheets, and molded products. Recently, we synthesized the alternating copolymers of RMIs containing a functional group, such as hydroxy and carboxy groups, combined with IB, and revealed the role of the intermolecular hydrogen bond of the functional groups in the thermal properties of the obtained copolymers.[22] We demonstrated that

poly(RMI-*alt*-IB)s containing hydroxy and carboxy groups showed high glass transition temperature (T_g) values depending on the structure of the *N*-substituents. However, the T_g values were insensitive to the position of the polar group, while the carbon skeleton structure of the *N*-alkyl substituents was important. For example, the T_g values were reported to be 139, 126, 124, and 154 °C for poly(RMI-*alt*-IB)s with 2-hydroxyethyl, 3-hydroxypropyl, 2-hydroxypropyl, and 1-methyl-2-hydroxyethyl groups as *N*-substituents, respectively.[22] In the present study, the alternating copolymers of *N*-(substituted phenyl)maleimides (XPhMIs), such as *N*-(hydroxyphenyl)-maleimides (**2–4**) and *N*-(4-carboxyphenyl)maleimide (**5**), with IB [poly(XPhMI-*alt*-IB)s] were synthesized, as shown in Scheme 1. The effects of hydroxy and carboxy groups on their thermal properties were investigated on the basis of the results of thermal analysis, temperature-controlled IR spectroscopy, and theoretical calculations. The rigid *N*-substituents of XPhMIs are expected to induce the intrinsic features of the copolymers containing polar groups at a fixed position.

EXPERIMENTAL

General Procedures

Number-average molecular weight (M_n), weight-average molecular weight (M_w), and polydispersity (M_w/M_n) were determined by gel permeation chromatography (GPC) in tetrahydrofuran (THF) as the eluent using a Tosoh CCPD RE-8020 system and calibration with standard polystyrenes. NMR spectra were recorded on a JEOL JMN A-400 spectrometer at room temperature using DMSO-d_6 as a solvent. Thermogravimetric and differential thermal analyses (TGA and

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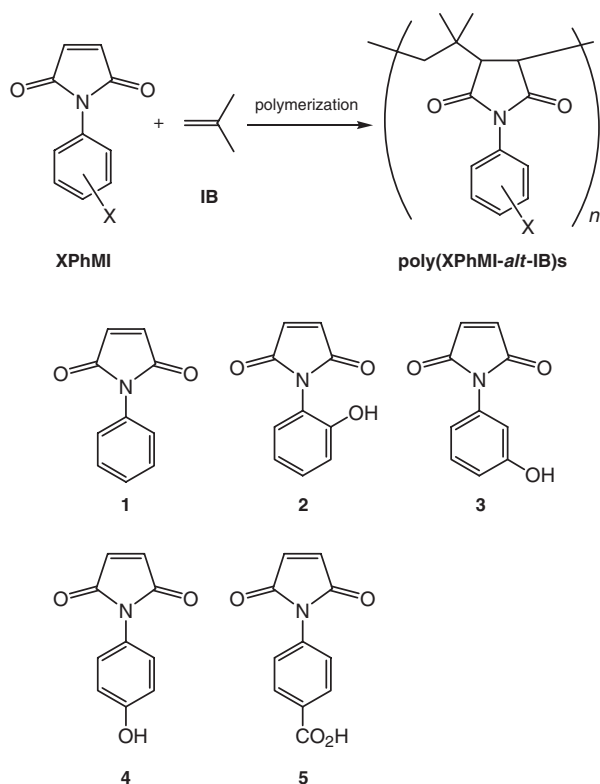
Scheme 1.

DTA, respectively) were carried out using a Seiko TG/DTA 6200 in a nitrogen stream at the heating rate of 10 °C/min. T_{init} and T_{max} values were determined as the onset and maximum rate temperatures of decomposition, respectively, using the derivatives of the TGA curves. T_{50} value was determined as the temperature at which the 50% of weight loss was observed. Differential scanning calorimetry (DSC) was carried out using a Seiko DSC-6200 at the heating rate of 10 °C/min to determine the T_g. Transmission IR spectra were recorded using a JASCO Herschel FT-IR-430 spectrometer. An Irtron IRT-30 system combined with a Mettler-Toledo FP900 controller was used for temperature-controlled IR measurement. The spectra were recorded at each 10 °C step on heating at the rate of 2 °C/min. UV-vis spectra were recorded using a JASCO V-550 spectrophotometer. DFT calculations were carried out at the (RO)B3LYP/6-311G*//(U)B3LYP/6-311G* level of theory using a Spartan'07 program.

Materials

2,2′-Azobis(4-methoxy-2,4-dimethylvaleronitrile) (AMVN) (Wako Pure Chemical Ind., Ltd., Osaka) was recrystallized from methanol. Commercially available **1** was used after recrystallization from ethanol. XPhMIs, **2–5**, were prepared according to the methods reported in the literature.[4,23–25] **2–4** were purified by silica gel column chromatography with a mixture of dichloromethane and ethyl acetate (10/1 in volume ratio), followed by recrystallization from the same solvents. **5** was recrystallized from a mixture of methanol and water (6/1

in volume ratio).

N-(2-Hydroxyphenyl)maleimide (**2**): Yield 11%, mp 146 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.82 (s, OH, 1H), 7.27 (td, $J = 7.4$ and 1.2 Hz, 4H of C_6H_4, 1H), 7.17 (s, CH=CH, 2H), 7.13 (dd, $J = 7.8$ and 1.2 Hz, 6H of C_6H_4, 1H), 6.93 (dd, $J = 8.0$ and 1.2 Hz, 3H of C_6H_4, 1H) 6.87 (ddd, $J = 7.2$, 8.0, and 1.6 Hz, 5H of C_6H_4, 1H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 170.17 (C=O), 154.00 (2C of C_6H_4), 134.99 (CH=CH), 130.43 (6C of C_6H_4), 130.24 (4C of C_6H_4), 119.14 (5C of C_6H_4), 118.59 (1C of C_6H_4), 116.48 (3C of C_6H_4); IR (KBr) $\nu_{C=O} = 1707$ cm^{-1}, $\nu_{O-H} = 3380$ cm^{-1}; UV (THF) $\lambda_{max} = 274$ nm ($\varepsilon = 6,880$).

N-(3-Hydroxyphenyl)maleimide (**3**): Yield 57%, mp 139 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.71 (s, H, 1H), 7.25 (t, $J = 8.4$ Hz, 5H of C_6H_4, 1H), 7.15 (s, CH=CH, 2H), 6.75–6.77 (m, 2H, 4H and 6H of C_6H_4, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 169.90 (C=O), 157.62 (3C of C_6H_4), 134.60 (CH=CH), 132.46 (1C of C_6H_4), 129.51 (5C of C_6H_4), 117.26 (6C of C_6H_4), 114.74 (4C of C_6H_4), 113.80 (2C of C_6H_4); IR (KBr) $\nu_{C=O} = 1698$ cm^{-1}, $\nu_{O-H} = 3327$ cm^{-1}; UV (THF) $\lambda_{max} = 278$ nm ($\varepsilon = 6,660$).

N-(4-Hydroxyphenyl)maleimide (**4**): Yield 93%, mp 188 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.71 (s, OH, 1H), 7.14 (s, CH=CH, 2H), 7.09 (d, $J = 8.8$ Hz, 3H and 5H of C_6H_4, 2H), 6.84 (d, $J = 8.8$ Hz, 2H and 6H of C_6H_4, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 170.35 (C=O), 157.06 (4C of C_6H_4), 134.53 (CH=CH), 128.47 (2C and 6C of C_6H_4), 122.53 (1C of C_6H_4), 115.45 (3C and 5C of C_6H_4); IR (KBr) $\nu_{C=O} = 1703$ cm^{-1}, $\nu_{O-H} = 3483$ cm^{-1}; UV (THF) $\lambda_{max} = 278$ nm ($\varepsilon = 5,980$).

N-(4-Carboxyphenyl)maleimide (**5**): Yield 89%, mp 242 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.1 (broad, CO$_2$H, 1H), 8.05 (d, $J = 8.8$ Hz, 3H and 5H of C_6H_4, 2H), 7.49 (d, $J = 8.8$ Hz, 2H and 6H of C_6H_4, 2H), 7.23 (s, CH=CH, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 169.90 (CO$_2$H), 167.02 (C=O), 135.82 (1C of C_6H_4), 135.18 (CH=CH), 130.21 (3C and 5C of C_6H_4), 129.85 (4C of C_6H_4), 126.46 (2C and 6C of C_6H_4); IR (KBr) $\nu_{C=O} = 1712$ cm^{-1}, $\nu_{O-H} = 3430$ cm^{-1}; UV (THF) $\lambda_{max} = 252$ nm ($\varepsilon = 36,700$).

Polymerization

An XPhMI monomer (2.0 mmol) and AMVN (0.10 mmol) in a mixture of 1,2-dichloroethane (5 mL) and methanol (5 mL) or in 1,4-dioxane (10 mL) were placed in a glass ampoule. The solution was degassed by the freeze-thaw technique. The cycle was repeated three times, and then IB was weighed and charged into the ampoule by vacuum distillation. Finally the ampoule was sealed. After polymerization at 30 °C for 5 h, the polymerization mixture was poured into a large amount of methanol or diethyl ether to precipitate the resulting poly(**1**-*alt*-IB) and the other poly(XPhMI-*alt*-IB)s, respectively. The copolymer was filtered, washed, and then dried *in vacuo*. The yield of the copolymer was gravimetrically determined. Poly(**1**-*alt*-IB) was purified by reprecipitation from chloroform and methanol. The other poly(XPhMI-*alt*-IB)s were similarly purified by reprecipitation from THF and diethyl ether. The

Table I. Synthesis and thermal properties of poly(XPhMI-*alt*-IB)s[a]

XPhMI	X	Yield[b] (%)	$M_n \times 10^{-4}$	$M_w \times 10^{-4}$	M_w/M_n	XPhMI mol %[c]	T_{init} (°C)	T_{max} (°C)	T_{50} (°C)	T_g (°C)
1	H	75	10.4	33.6	3.2	48.0	365	438	434	186
2	2-OH	73	2.2	6.6	2.9	49.4	349	395	394	222
3	3-OH	76	4.8	7.2	1.5	49.6	371	408	409	223
4	4-OH	83	4.2	10.2	2.4	49.0	365	419	417	232
5	4-CO$_2$H	54	14.0	44.7	3.1	49.9	375	424	480	259

[a]Copolymerization conditions: [XPhMI] = 0.20 mol/L, [IB] = 2.0 mol/L, [AMVN] = 10 mmol/L in 1,2-dichloroethane and methanol (1:1 in volume ratio) for the copolymerization of **2–5**, and in 1,4-dioxane for **1** at 30 °C for 5 h. [b]Calculated on basis of XPhMI. [c]In copolymer, determined by ^{1}H NMR spectroscopy.

composition of the obtained copolymers was determined by ^{1}H NMR spectroscopy.

RESULTS AND DISCUSSION

The radical copolymerization of **2–5** was carried out using a large excess of IB in a mixture of 1,2-dichloroethane and methanol and that of **1** with IB in 1,4-dioxane. All the copolymerization systems were apparently homogeneous, although the resulting copolymers were insoluble in the same solvent after isolation. The results of the copolymerization are summarized in Table I. The copolymers with a high molecular weight ($M_n = 2–14 \times 10^4$) were obtained in yields of 54–83% during the copolymerization at 30 °C for 5 h. The copolymers isolated after reprecipitation were a colorless powder, except for poly(**4**-*alt*-IB) which was pale brown. The alternating repeating structure of the copolymers was confirmed by ^{1}H NMR spectroscopy (Figure 1), similar to the results for the copolymerization of *N*-alkyl- and *N*-(alkyl-substituted phenyl)maleimides with IB.[13,18] The steric hindrance of the substituents in the ortho-substituted XPhMIs decreases their propagation rate constants and relative monomer reactivity during homo- and copolymerizations, respectively, according to the number and size of the substituents.[14,26,27] Consequently, alternating copolymers are readily produced during the copolymerization of the ortho-substituted XPhMIs with IB because of a lack of the homopolymerizability of IB. In the present study, the alternating copolymers of XPhMI and IB were obtained irrespective of the position of polar substituents in the phenyl group, during copolymerization under the conditions with a large excess of IB.

The solubility of the copolymers is summarized in Table II. Poly(XPhMI-*alt*-IB)s were soluble in polar solvents, such as DMSO, DMF, and THF, and insoluble in toluene, *n*-hexane, diethyl ether, ethyl acetate, and water. The copolymers having polar hydroxy and carboxy groups were also soluble in acetone and insoluble in halogen-containing solvents, such as 1,2-dichloroethane and chloroform, while poly(**1**-*alt*-IB) was soluble in the same halogen-containing solvents and swollen with acetone. Poly(**2**-*alt*-IB), which has a 2-hydroxy substituent, was swollen in methanol, but the other poly(XPhMI-*alt*-IB)s were insoluble in methanol without any swelling. Poly(**3**-*alt*-IB) and poly(**4**-*alt*-IB) showed the same solubility. Thus,
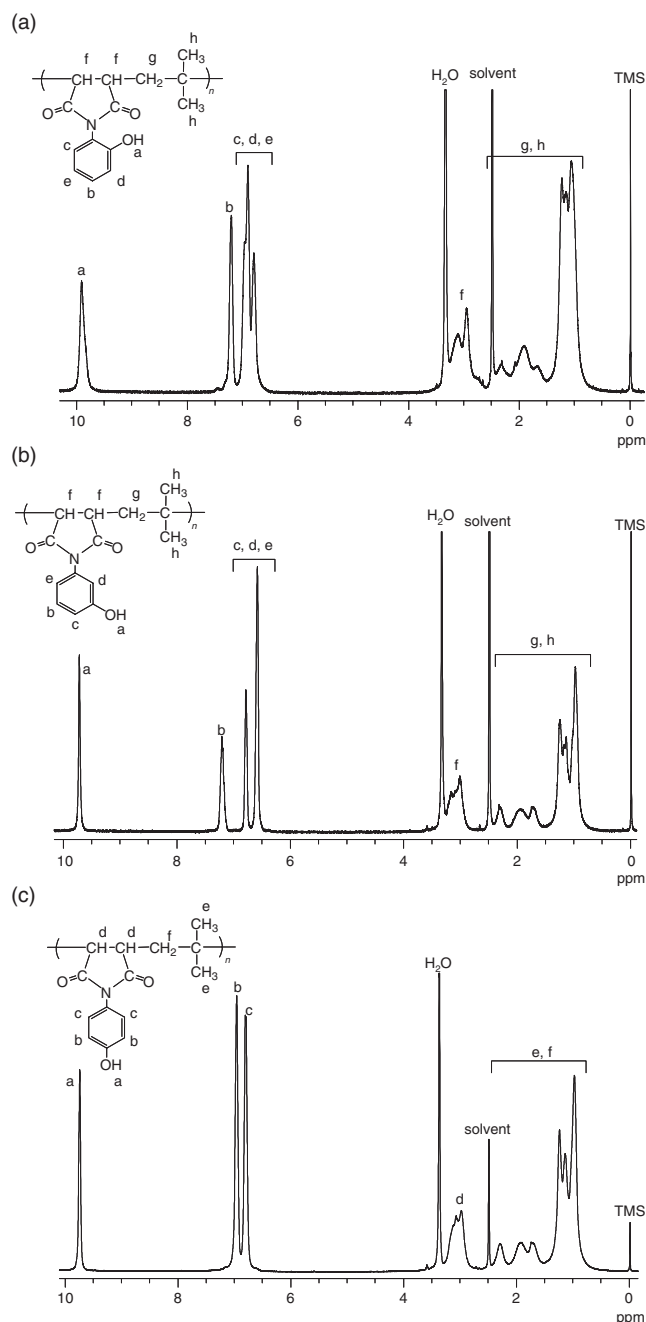

Figure 1. ^{1}H NMR spectra of (a) poly(**2**-*alt*-IB), (b) poly(**3**-*alt*-IB), and (c) poly(**4**-*alt*-IB) in DMSO-d_6 at room temperature.

Table II. Solubility of poly(XPhMI-*alt*-IB)s at room temperature

| Polymer	DMSO, DMF, THF	Acetone	Chloroform	1,2-Dichloroethane	Methanol
Poly(**1**-*alt*-IB)	soluble	swelling	soluble	soluble	insoluble
Poly(**2**-*alt*-IB)	soluble	soluble	insoluble	insoluble	swelling
Poly(**3**-*alt*-IB)	soluble	soluble	swelling	insoluble	insoluble
Poly(**4**-*alt*-IB)	soluble	soluble	swelling	insoluble	insoluble
Poly(**5**-*alt*-IB)	soluble	soluble	insoluble	insoluble	insoluble
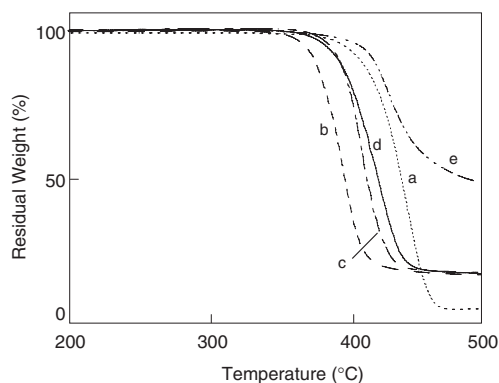
Figure 2. TGA curves of poly(XPhMI-*alt*-IB)s in a nitrogen stream at the heating rate of 10 °C/min. (a) poly(**1**-*alt*-IB), (b) poly(**2**-*alt*-IB), (c) poly(**3**-*alt*-IB), (d) poly(**4**-*alt*-IB), and (e) poly(**5**-*alt*-IB).

the solubility of poly(XPhMI-*alt*-IB)s substituted with a polar group is importantly different from that of poly(**1**-*alt*-IB) and slightly depended on the position and structure of the polar groups. Transparent and brittle films were obtained from all poly(XPhMI-*alt*-IB)s by casting from their acetone solutions.

The thermal stability of poly(XPhMI-*alt*-IB)s was examined by TGA in a nitrogen stream at the heating rate of 10 °C/min. The obtained TGA curves are shown in Figure 2. The determined T_{init}, T_{max}, and T_{50} values are summarized in Table I. The thermal decomposition of all poly(XPhMI-*alt*-IB)s proceeded *via* a one-step reaction, and no weight-loss was observed below 350 °C. The decomposition temperatures for poly(XPhMI-*alt*-IB)s, $T_{init} = 349$–375 °C and $T_{max} = 395$–438 °C, were similar to those for poly(*N*-alkylmaleimide-*alt*-IB)s; $T_{init} = 327$–382 °C and $T_{max} = 390$–449 °C. The T_{init} and T_{50} values of poly(**5**-*alt*-IB) were the highest among those of the poly(XPhMI-*alt*-IB)s examined in the present study. The residual weight at 500 °C for poly(**5**-*alt*-IB) was 48%, which was much greater than those for the other poly(XPhMI-*alt*-IB)s. The decomposition of the hydroxy-substituted poly-(XPhMI-*alt*-IB)s occurred at a temperature similar to or slightly lower than the decomposition temperature of poly(**1**-*alt*-IB). The residual weight of the hydroxy-substituted polymers was 16%, independent of the position of the hydroxy group. Thus, poly(XPhMI-*alt*-IB)s containing the hydroxy and carboxy groups resulted in a larger amount of residue after decomposition rather than poly(**1**-*alt*-IB) because of some reactions occurring between the substituents on the *N*-phenyl group during thermal decomposition. For example, the carboxy groups form the anhydride upon heating, and the intermolecular binding between the polymer chains may further induce the formation of a graphite-like thermally stable structure rather than fragmentation. As a result, a large part of polymers were charred and isolated as the residue after the heating to 500 °C. However, the analysis of the residue gave no useful information regarding a detailed mechanism for the decomposition reaction and the structure of the products. A similar behavior was also observed during the decomposition of the other poly(XPhMI-*alt*-IB)s with alkyl and alkoxycarbonyl substituents.[14,15]

Poly(XPhMI-*alt*-IB)s containing hydroxy and carboxy groups showed the T_g values of 222–232 °C and 259 °C, respectively, which are much higher than that of poly(**1**-*alt*-IB) ($T_g = 186$ °C), as summarized in Table I. This result suggests that an increase in the T_g values of poly(XPhMI-*alt*-IB)s is due to intermolecular hydrogen bonding between the hydroxy and carboxy groups. Furthermore, the introduction of the functional groups into the para position of the *N*-phenyl ring was effective for an increase in the T_g value of the copolymers, while poly(**2**-*alt*-IB) and poly(**3**-*alt*-IB) showed the identical T_g values. In general, the T_g of polymers depends on the steric bulkiness of substituents in the side chain, as well as the strength of dipole and intermolecular interactions. For example, higher T_g values were reported for the vinyl polymers containing any substituent near the main chain, such as the 2-position of a phenyl or cycloalkyl group in the side chain.[28–30] Considering a steric factor, poly(**2**-*alt*-IB) was expected to show the highest T_g value due to the steric hindrance, but actually this was not true. In a previous paper,[18] the T_g values of poly(XPhMI-*alt*-IB) containing 2-methyl and 2,6-dimethyl substituents in the *N*-phenyl group were reported to be 207 and 237 °C, respectively. The T_g value (222 °C) for poly(**2**-*alt*-IB) in the present study was higher than that of the 2-methyl-substituted one. The suppressed chain mobility of the 2,6-disubstituted derivative results in a higher T_g value because of the rigid conformation of the *N*-phenyl ring in the side chain.[14] In the literature, no report on the effect of the position of the alkyl-substituent on the T_g values for the poly(XPhMI-*alt*-IB) has been found. In order to further examine the role of the functional groups in the present study, the intermolecular interaction of the functional groups of poly(XPhMI-*alt*-IB)s through hydrogen bonding was investigated by IR spectroscopy under temperature control.

First, the intermolecular hydrogen bonding was examined. Figure 3 shows a change in the absorption bands due to the O–H stretching vibration at 3460 cm^{-1} and the C=O stretching at 1698 cm^{-1} in the IR spectrum of poly(**4**-*alt*-IB). Upon heating from 100 to 300 °C, an intermolecular interaction between the hydroxy groups was reduced, and accordingly, the average position of the OH band shifted to a higher wavenumber region. On the other hand, no change was observed for the position of the C=O band. Similar results were also obtained for poly(**2**-*alt*-IB) and poly(**3**-*alt*-IB). Figure 4 shows the comparison of the change in the position and the intensity of the OH bands for poly(**2**-*alt*-IB), poly(**3**-*alt*-IB), and poly(**4**-*alt*-IB). For poly(**2**-*alt*-IB), the wavenumber of the peak linearly increased and the intensity linearly decreased as the temperature increased in the whole temperature range examined. In contrast, the wavenumber and the intensity of the peak for the OH band of poly(**4**-*alt*-IB) remained constant below *ca.* 200 °C and then drastically changed at a higher temperature. In the spectrum of poly(**3**-*alt*-IB), the peak intensity discontinuously decreased, while the peak position shifted to a higher wavelength region during heating to the temperature around the T_g and then it kept constant over the T_g. These results suggest that the function of the hydrogen bonding of the hydroxy group of poly(**2**-*alt*-IB) is different from the others. This is because
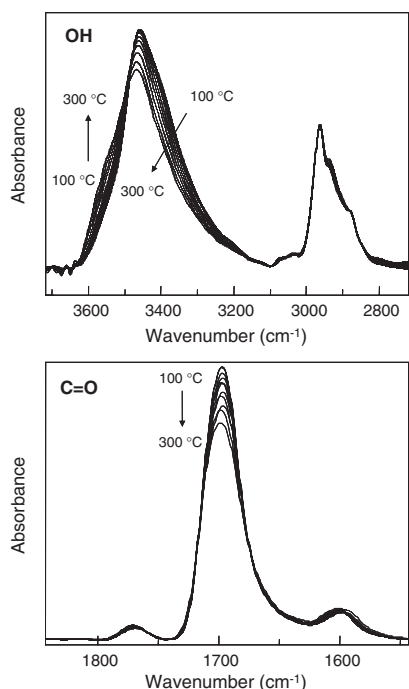
Figure 3. Change in the hydroxy and carbonyl regions of the IR spectrum for poly(**4**-*alt*-IB) upon heating. The spectra are normalized by the intensity of the C–H band at 2963 cm^{-1} and shown at each 20 °C step upon heating at the rate of 2 °C/min.
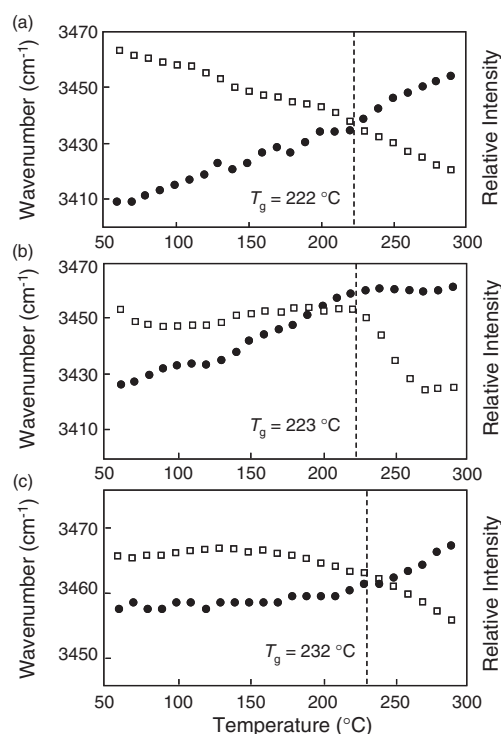

Figure 4. Change in the wavenumber (●) and intensity (□) of the peak due to the hydroxy group in the IR spectra of (a) poly(**2**-*alt*-IB), (b) poly(**3**-*alt*-IB), and (c) poly(**4**-*alt*-IB) upon heating at the rate of 2 °C/min.

the intermolecular hydrogen bonding is closely related to the determination of the T_g values for poly(**3**-*alt*-IB) and poly(**4**-*alt*-IB) and it is drastically weakened in the temperature range over the T_g. In contrast, the hydrogen bonding of poly(**2**-*alt*-IB) does not influence polymer dynamics below and over the T_g value. This is due to the intramolecular hydrogen bonding between the hydroxy and the maleimide carbonyl groups in the same repeating unit, which linearly becomes weak depending on the temperature. The formation of intramolecular hydrogen bonding for poly(**2**-*alt*-IB) is discussed in the later section on the basis of the results of DFT calculations.

The intermolecular hydrogen bonding of poly(XPhMI-*alt*-IB)s includes several possible cases, such as hydroxy–hydroxy and hydroxy–carbonyl interactions for the hydroxy-substituted poly(XPhMI-*alt*-IB)s, and carboxy–carboxy and carboxy–carbonyl interactions for poly(**5**-*alt*-IB). Actually no shift was detected in the absorption band of the carbonyl group, but it is due to an insensitive peak shift for the C=O of the maleimide ring in the IR spectrum.[22] In the case of the hydroxy-substituted poly(XPhMI-*alt*-IB)s, it is consider that the intermolecular hydrogen bonding of poly(XPhMI-*alt*-IB)s include not only hydroxy–hydroxy but also hydroxy–carbonyl interactions.

We also tried to reveal the intermolecular interaction of the functional group of poly(**5**-*alt*-IB) to investigate the carboxy–carboxy and carboxy–carbonyl interactions as intermolecular hydrogen bonding. The absorption band due to the O–H stretching of the carboxy group was observed at 3000–3500 cm^{-1} and shifted to a higher wavenumber region when the temperature increased over the T_g, similar to the results for the
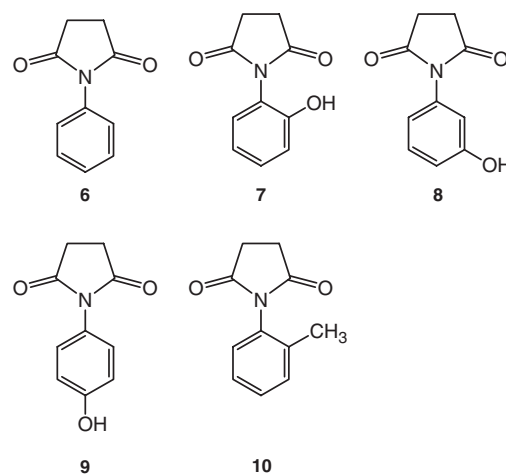
Scheme 2.

hydroxy group in poly(XPhMI-*alt*-IB)s. However, the analysis of the C=O band failed because of the overlap of two kinds of C=O absorptions, due to the C=O stretching of the CO$_2$H group in the *N*-substituent and the symmetric C=O stretching of the maleimide ring, appearing at 1712 cm^{-1}.

Next, the optimized molecular structure of **1**–**4** as well as the corresponding succinimides (**6**–**9**) as model compounds for the polymer repeating unit (Scheme 2) were determined by DFT calculations at the (RO)B3LYP/6-311G*//(U)B3LYP/6-311G* level of theory. Figure 5 shows the optimized molecular conformations of **7**–**9**, together with an electrostatic potential
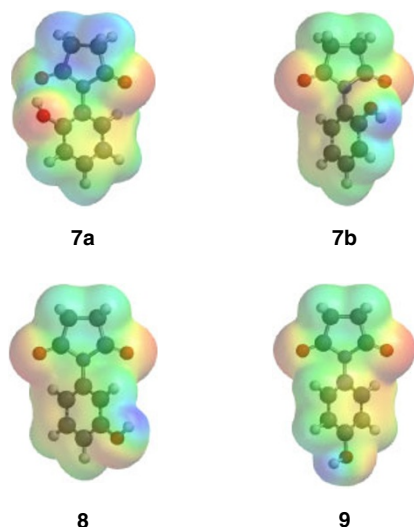
7a　　　　**7b**

8　　　　**9**

Figure 5. Optimized molecular conformations and electrostatic potential map on the molecular surface determined by DFT calculations for **7–9** as the model compounds for the maleimide repeating unit in poly(XPhMI-*alt*-IB)s. Compound **7** has two stable conformers, **7a** and **7b**. In an electrostatic potential map, red and blue depict the most negative and positive potentials, respectively. Orange, yellow, and green colors depict intermediate values, according to the sign and magnitude of the potentials.

Table III. Structural parameters for maleimide and succinimide derivatives determined by DFT calculations[a]

Compound		ΔH^b (kJ/mol)	Dihedral angle[c] (°)	N–C bond angle[d] (°)
Maleimide	**1**	—	45.2	0
	2a	0	45.2	0.7
	2b	12.38	74.4	5.5
	3	6.56	37.5	0.1
	4	7.23	43.8	0.1
Succinimide	**6**	—	44.3	0
	7a	0	46.7	0.2
	7b	15.51	71.1	2.7
	8	10.42	41.2	0.2
	9	10.27	43.4	0.1
	10	—	64.8	2.8

[a]Calculated by DFT method at the (RO)B3LYP/6-311G*//(U)B3LYP/6-311G* level of theory. [b]Relative value for the heat of formation. [c]Angle between the imide and *N*-phenyl rings. [d]Angle between the imide ring and the N–C bond.

map on molecular surface. Some parameters determined for the optimized structures of each isomer are summarized in Table III.

Compound **7** was revealed to have two stable conformations, **7a** and **7b**, one of which includes intramolecular hydrogen bonding between the hydroxy group on the ortho position of the *N*-phenyl ring and the imide carbonyl group. The bond length between the hydrogen atom of the OH group and the oxygen atom of the C=O group of **7a** was 1.8 Å, and the O–H···O angle was 152.5°. This geometry strongly supports that intramolecular hydrogen bonding is formed in **7a**. The formation of an intramolecular hydrogen bonding between the OH and C=O groups in the conformer **7a** is also evident from its electrostatic potential map, in which a decrease in the electron density for one of the C=O groups. Another

conformer, **7b**, contains a highly twisted *N*-phenyl ring structure without intramolecular hydrogen bonding.[14,31,32] The dihedral angles between the imide and *N*-phenyl ring were 41.2–44.3° for the compounds, **6**, **8**, and **9**, and 46.7° for **7a**. The steric hindrance due to the ortho-substitution resulted in the more twisted structures when the intramolecular hydrogen bonding is absent, as seen in the dihedral angles of 71.1 and 64.8° for **7b** and **10**, respectively. The steric strain included in the **7b** and **10** molecules was also reflected in the tilted structure of the *N*-phenyl substituent from the imide plane; the angle between the imide ring and the N–C bond was 2.7 and 2.8° for **7b** and **10**, respectively, being larger than those for the other derivatives (0–0.2°). The maleimide derivatives, **1–4**, also resulted in similar conclusions. The dihedral angles between the phenyl and imide rings were determined to be 38–45° for the maleimide derivatives when intramolecular hydrogen bonding and the steric hindrance of the ortho substituent are absent. The conformer **2b** has a highly twisted and strained structure due to the steric repulsion.

As shown in Table III, the highly twisted conformers, **2b** and **7b**, are energetically unfavorable ($\Delta H = 12.38$ and 15.51 kJ/mol for **2b** and **7b**, respectively) compared with another conformers, **2a** and **7a**. The relative enthalpy values for **2b** and **7b** are approximately 5 kJ/mol higher than those of the other hydroxy substituted structures; $\Delta H = 6.6$–7.2 and 10.3–10.4 kJ/mol for the maleimide (**3** and **4**) and succinimide (**8** and **9**) derivatives, respectively. Judging from the energy difference between the two conformers for each compound, we can conclude that a molecular conformation containing intramolecular hydrogen bonding, which are similar to those of conformers **2a** and **7a**, is predominant as the repeating structure of poly(**2**-*alt*-IB). The temperature dependence of the OH band in the IR spectrum of poly(**2**-*alt*-IB), as already shown in Figure 4, is well accounted for by the predominant intramolecular hydrogen bonding between the 2-OH group and the carbonyl group.

In conclusion, we demonstrated that the alternating copolymers obtained from XPhMI having hydroxy and carboxy substituents and IB, poly(XPhMI-*alt*-IB)s, show excellent thermal stabilities. The T_g values of poly(XPhMI-*alt*-IB)s depended on the structure and position of the polar groups on the *N*-phenyl group. The role of intermolecular and intramolecular hydrogen bonding for determining the T_g values was revealed by temperature-controlled IR spectroscopy. The molecular conformation determined by DFT calculations has clarified that the rigid *N*-substituents of the XPhMI units induce the intrinsic features of the copolymers containing the polar groups at a fixed position. The results obtained in the present study will be useful for the synthesis of thermo-resistant polymers with an excellent transparency including aromatic polyimides, as well as the design of π-conjugated polymers and oligomers.

REFERENCES

1. M. Barrales-Rienda, J. I. G. De la Campa, and J. G. Ramos, *J. Macromol. Sci. Chem.*, **A11**, 267 (1977).
2. T. Otsu, A. Matsumoto, T. Kubota, and S. Mori, *Polym. Bull.*, **23**, 43 (1990).
3. D. J. T. Hill, L. Y. Shao, P. J. Pomery, and A. K. Whittaker, *Polymer*, **42**, 4791 (2001).
4. M. J. Caulfield and D. H. Solomon, *Polymer*, **40**, 1251 (1999).
5. T. Oishi, Y. Otsubo, K. Matsusaki, and M. Fujimoto, *Polymer*, **34**, 1504 (1993).
6. K.-D. Ahn, D.-I. Koo, and C. G. Willson, *Polymer*, **36**, 2621 (1995).
7. C. Soykan and I. Erol, *J. Appl. Polym. Sci.*, **91**, 964 (2004).
8. C. P. R. Nair, D. Mathew, and K. N. Ninan, *Eur. Polym. J.*, **35**, 1829 (1999).
9. W. Y. Chiang and J. Y. Lu, *J. Appl. Polym. Sci.*, **50**, 1007 (1993).
10. A. Matsumoto, K. Hasegawa, and A. Fukuda, *Polym. Inter.*, **30**, 65 (1993).
11. D. Mathew, C. P. R. Nair, and K. N. Ninan, *Eur. Polym. J.*, **36**, 1195 (2000).
12. T. Oishi, Y. Isobe, K. Onimura, and H. Tsutsumi, *Polym. J.*, **35**, 245 (2003).
13. T. Doi, A. Akimoto, A. Matsumoto, Y. Oki, and T. Otsu, *J. Polym. Sci., Part A: Polym. Chem.*, **34**, 2499 (1996).
14. A. Matsumoto, T. Kubota, and T. Otsu, *Macromolecules*, **23**, 4508 (1990).
15. A. Matsumoto and T. Kimura, *J. Appl. Polym. Sci.*, **68**, 1703 (1998).
16. S. Amou, S. Nishimura, A. Takahashi, T. Hagiwara, H. Hamana, and T. Narita, *J. Polym. Sci., Part A: Polym. Chem.*, **37**, 341 (1999).
17. T. Oishi, M. Iwahara, and M. Fujimoto, *Polym. J.*, **23**, 1409 (1991).
18. T. Doi, A. Akimoto, A. Matsumoto, and T. Otsu, *J. Polym. Sci., Part A: Polym. Chem.*, **34**, 367 (1996).
19. T. Doi, Y. Sugiura, S. Yukioka, and A. Akimoto, *J. Appl. Polym. Sci.*, **61**, 853 (1996).
20. T. Doi, N. Ishikawa, and A. Akimoto, *J. Appl. Polym. Sci.*, **61**, 859 (1996).
21. T. Doi, S. Yukioka, H. Inoue, and A. Akimoto, *J. Appl. Polym. Sci.*, **63**, 925 (1997).
22. A. Omayu, T. Ueno, and A. Matsumoto, *Macromol. Chem. Phys.*, in press.
23. J. E. White, D. S. Mark, and A. S. Deborah, *J. Appl. Polym. Sci.*, **29**, 891 (1984).
24. T. Oishi and M. Fujimoto, *J. Polym. Sci., Part A: Polym. Chem.*, **30**, 1821 (1992).
25. A. Matsumoto, Y. Oki, and T. Otsu, *J. Macromol. Sci. Chem.*, **A29**, 831 (1992).
26. A. Matsumoto, Y. Oki, and T. Otsu, *Macromolecules*, **25**, 3323 (1992).
27. A. Matsumoto, Y. Oki, and T. Otsu, *Eur. Polym. J.*, **29**, 1225 (1993).
28. B. Yamada, A. Matsumoto, and T. Otsu, *Makromol. Chem.*, **192**, 1921 (1991).
29. A. Matsumoto and K. Mizuta, *Polym. Bull.*, **33**, 141 (1994).
30. P. Camelio, V. Lazzeri, and B. Waegell, *Macromolecules*, **31**, 2305 (1998).
31. T. Matsuo, *Bull. Chem. Soc. Jpn.*, **38**, 557 (1965).
32. T. Matsuo, *Bull. Chem. Soc. Jpn.*, **37**, 1844 (1964).