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SYNTHESIS AND RADICAL POLYMERIZATION OF BIFUNCTIONAL MALEIMIDES WITH DIFFERENT FUNCTIONAL REACTIVITIES

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ABSTRACT

Three bifunctional *N*-phenylmaleimide derivatives, *N*-[4-(2-hydroxy-3-methacryloyloxy propyloxycarbonyl)phenyl]maleimide (GMAPMI, **1**), *N*-(4-methacryloyloxyphenyl) maleimide (MAPMI, **2**) and 4-(4-maleimidobenzoyloxy)styrene (MIBOSt, **3**) having radically polymerizable maleimide and vinyl groups together have been synthesized and polymerized. Polymerizations of the bifunctional maleimide monomers were carried out using a radical initiator at 55°C and the results were compared

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with those obtained by self-polymerization in the absence of initors. All of the polymers obtained were insoluble in organic solvents owing to cross-linking between different functional groups. The reactivity for homopolymerization of monomer **3** is higher than that of monomers **1** and **2** because the styryl moiety of monomer **3** has better electron-donor strength than the methacrylate moiety. Under the same conditions, GMAPMI was copolymerized with *N*-vinyl-2-pyrrolidone and styrene as an electron-donor to give higher conversions by electron-donor/acceptor polymerization in which the maleimide moiety of GMAPMI mainly involved as an electron acceptor.

INTRODUCTION

Bifunctional monomers possessing two polymerizable vinyl groups are of particular interest for the study of complex radical polymerization and for designing functional polymers to obtain desired composition, structure and properties [1]. This type of radical polymerization involving different polymerization reactivities will lead to a new avenue for polymer reactions and macromolecular network formation [2]. It is known that *N*-substituted maleimides having polymerizable carbon-carbon double bonds with different reactivities were able to selectively polymerize by variation of the initiators [3, 4]. The electron-deficient *N*-substituted maleimides as an electron-acceptor undergo alternating copolymerization with or without using radical initiators when copolymerized with electron-donor monomers such as styrene and vinyl ether derivatives through electron-donor/acceptor (EDA) polymerization [5-7]. Hult *et al.* [8] reported a unique EDA polymerization system in which bifunctional *N*-phenylmaleimides containing a vinyl ether moiety were carefully prepared as a liquid crystalline EDA monomer and photopolymerized without externally added photoinitiators. A maleimide moiety also acts as a dienophile undergoing thermal curing easily by a Diels-Alder reaction [9]. Such versatile reactions in bifunctional maleimides are very useful for modification and curing of polymers.

We have continuously been involved in the studies on functional polymaleimides obtained by EDA polymerization, particularly, for application to photolithography based on the chemical amplification concept [10, 11]. N-Substituted functional maleimides have been studied as versatile vinyl monomer with desired functionalities offering great flexibility in designing and synthesis [12, 13]. Our initial efforts have concentrated on tailoring predesigned bifunctional maleimide derivatives to achieve a specific EDA polymerization system.

The relatively low homopolymerizability of maleimide moieties allows us to speculate that reasonably efficient thermal and photopolymerization systems might be developed based on bifunctional maleimide monomers containing electron-donor groups within the same molecule.

In this paper, we report the synthesis and radical polymerization of three bifunctional *N*-phenylmaleimide monomers which simultaneously possess a methacryloyl or a styryl moiety for the sake of different polymerization behaviors. Their copolymerizations with *N*-vinyl-2-pyrrolidinone, styrene, and methyl methacrylate were also investigated in view of EDA-type polymerization.

EXPERIMENTAL

Materials and Instruments

Methyl methacrylate (MMA), *N*-vinyl-2-pyrrolidinone (NVP), glycidyl methacrylate (GMA), methacryloyl chloride, styrene (St) and 4-acetoxystyrene were purchased from Aldrich Chemical Co. The monomers and solvents such as 1,4-dioxane and tetrahydrofuran (THF) were purified by fractional distillation or recrystallization before use. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian Gemini 200 spectrometer of Perkin-Elmer using CDCl$_3$. Infrared spectra were recorded on a Polaris FT-IR spectrophotometer from Mattson Instrument Co. Thermal properties of polymers were analyzed by Model DSC 910 and Model 951 TGA of TA Instruments, Inc. UV spectra were recorded on a JASCO Model V530 UV-Vis spectrophotometer. Mass spectra were obtained with a Finnigan SSQ 7000. Elemental analysis were done with a Fisons Instrument EA1108 elemental analyzer.

Synthesis of *N*-[4-(2-Hydroxy-3-methacryloyloxypropyloxy-carbonyl)-phenyl]maleimide, GMAPMI (1)

N-(4-Carboxyphenyl)maleimide was prepared from *p*-aminobenzoic acid and maleic anhydride by the modified method as described in the literature [14]. To a solution containing 15.02 g (69.0 mmol) of *N*-(4-carboxy-phenyl)maleimide in 100 ml of dioxane added were 160 mg (0.7 mmol) of benzyltriethyl-ammonium chloride and 76 mg (0.7 mmol) of hydroquinone as a catalyst and as an inhibitor, respectively. Then, 9.82 g (0.7 mmol) of glycidyl methacrylate in 10 ml of dioxane were added dropwise to the solution at room temperature. The mixture was heated gradually up to 100°C and stirred for 3 days under nitrogen atmosphere. The reaction mixture was filtered to eliminate unreacted starting

materials and precipitates. The filtrate was concentrated under reduced pressure, and the residue was dissolved in ethyl acetate and washed with aqueous $NaHCO_3$ and NaCl solution. The organic phase was separated, dried over anhydrous magnesium sulfate and evaporated.   The residue was subjected to column chromatography on silica gel using ethyl acetate-hexane (6:4 by vol) as an eluent. The oily concentrate was crystallized from ethyl ether to obtain white granular crystals of GMAPMI (4.34 g, 18%), mp 74°C, λ max = 249 nm. ^{1}H NMR (200MHz, $CDCl_3$), δ (ppm): 8.11 (d, 2H, aromatic), 7.47 (d, 2H, aromatic), 6.86 (s, 2H, C$\underline{H}$=C$\underline{H}$ of maleimide), 6.13 (s, 1H, C=C$\underline{H}_2$ of methacrylate), 5.59 (s, 1H, C=C$\underline{H}_2$ of methacrylate), 4.40 ~ 4.41 (m, 2H, C$\underline{H}_2$CHCH$_2$), 4.29 ~ 4.40 (m, 1H, CH$_2$C$\underline{H}$CH$_2$), 4.29 ~ 4.40 (m, 1H, CH$_2$CHC$\underline{H}_2$), 3.03 (s, 1H, O$\underline{H}$), 1.93 (s, 3H, CC$\underline{H}_3$). ^{13}C NMR ($CDCl_3$), δ (ppm): 168.97 ($\underline{C}$=O of maleimide), 167.44 (C-$\underline{C}$=O), 165.75 (Ph-$\underline{C}$=O), 135.68 (aromatic), 134.40 ($\underline{C}$=$\underline{C}$ of maleimide), 130.55 (aromatic), 128.44 ($\underline{C}$=CH$_2$), 126.50 ($\underline{C}$=CH$_2$), 125.22 (aromatic), 68.12 (CH$_2$CH$\underline{C}$H$_2$), 65.81 ($\underline{C}$H$_2$CHCH$_2$), 65.37 ($\underline{C}$H$_2$CHCH$_2$), 18.14 (C$\underline{C}$H$_3$).   IR (KBr), ν (cm^{-1}): 3474 (OH stretching), 1717 (C=O of imide and ester stretching), 1635 (C=CH$_2$ stretching), 1608 (C=C of aromatic stretching), 1279 and 1119 (C-O bending), 830 (CH=CH of maleimide).   Anal. Calcd for $C_{18}H_{17}O_7N_1$ (359.34): C 60.17, H 4.77, N 3.90; Found C 59.40, H 4.70, N 3.85.

Synthesis of N-(4-Methacryloyloxyphenyl)maleimide, MAPMI (2)

N-(4-Hydroxyphenyl)maleimide was prepared from *p*-aminophenol and maleic anhydride by the method previously reported [15]. To a solution of *N*-(4-hydroxy phenyl)maleimide (15.00 g, 79 mmol) in 150 *ml* of acetone added was triethylamine (8.00 g, 79 mmol). To this solution of methacryloyl chloride 8.20 g, 79 mmol in 10 ml of acetone was dropwisely added for 30 minutes at 0°C. The resulting mixture was stirred at room temperature for 1 day under nitrogen atmosphere. The progress of the reaction was checked by thin-layer chromatography. Upon completion, the mixture was filtered and the filtrate was concentrated *in vacuo*. Recrystallization of the yellowish solid residue from a solution of acetone and n-hexane (2:5 by vol.) gave yellowish granular crystals of MAPMI (19.00 g, 82%), mp 160°C, $λ_{max}$ = 263 nm. ^{1}H-NMR (200 MHz, $CDCl_3$), δ (ppm): 7.38 (d, 2H, aromatic), 7.21 (d, 2H, aromatic), 6.80 (s, 2H, C$\underline{H}$=C$\underline{H}$- of maleimide), 6.34 (s, 1H, C=C$\underline{H}_2$ of methacrylate), 5.77 (s, 1H, C=C$\underline{H}_2$ of methacrylate), 2.05 (s, 3H, CC$\underline{H}_3$). ^{13}C NMR ($CDCl_3$), δ (ppm): 169.37 (C=O of maleimide), 1665.47 (C-C=O), 150.02 and 135.58 (aromatic), 134.17 (C=C of maleimide) 128.61 (C=CH$_2$), 127.59 (C=CH$_2$), 126.89, 122.27 (aromatic), 18.20

(CCCH$_3$). IR (Kbr), ν (cm^{-1}): 1717 (C=O of imide and ester stretching), 1638 (C=CH2 stretching), 1604 (C=C of aromatic stretching), 1294 and 1152 (C-O bending), 832 (CH=CH of maleimide). Anal. Calcd for C$_{14}$H$_{11}$O$_4$N$_1$ (257.25): C 65.37, H 4.31, N 5.45; found, C 64.70, H 4.31, N 5.32.

Synthesis of 4-(4-Maleimidobenzoyloxy)styrene, MIBOSt (3)

Thionyl chloride was reacted with the previously obtained *N*-(4-carboxyphenyl)maleimide to synthesize 4-maleimidobenzoyl chloride [16,17]. 4-Hydroxystyrene was obtained by hydrolysis of 4-acetoxystyrene [18]. A mixture of 4-maleimidobenzoyl chloride (1.00 g, 4.2 mmol) and 4-hydroxystyrene (0.51 g, 4.2 mmol) with triethylamine (0.43 g, 4.2 mmol) in 20 *ml* of THF was reacted for 3 hours at 5°C. The completion of the reaction was monitored by thin-layer chromatography. Recrystallization of the residue from THF after work-up by filtration and concentration of the filtrate yielded yellowish needle crystals of MIBOSt (1.25 g, 84%), mp 124°C, λ_{max} = 261 nm. ^{1}H NMR (200 MHz, CDCl$_3$), δ (ppm): 7.53 ~ 8.35 (4H, aromatic), 7.20 ~ 7.53 (4H, aromatic), 6.92 (s, 2H, C$\underline{H}$=C$\underline{H}$- of maleimide), 6.70 (d of d, 1H, C$\underline{H}$=C$\underline{H_2}$), 5.78 (d, 1H, CH=C$\underline{H_2}$), 5.31 (d, 1H, -CH=C$\underline{H_2}$). ^{13}C NMR (CDCl$_3$), δ (ppm): 168.87 ($\underline{C}$=O of maleimide), 164.29 (C-$\underline{C}$=O), 150.26, 135.98, 135.80, 135.45, 131.00, 128.28, 127.22 and 125.26 (aromatic), 134.40 ($\underline{C}$=$\underline{C}$ of maleimide), 121.67 ($\underline{C}$H=CH$_2$), 114.14 (CH=$\underline{C}$H$_2$).   IR (KBr), ν (cm^{-1}): 1742 and 1718 (C=O ester of stretching and imide), 1631 (C=CH$_2$ stretching), 1270 (C-O-C), 833 (CH=CH of maleimide).

Radical Polymerization

All of the radical homo- and copolymerizations for the monomers **1-3** were carried out in sealed ampoules after degassing by a freeze-thaw process with argon. *N,N′*-azobisisobutyronitrile (AIBN) purified by recrystallization from methanol was used as a radical initiator. After polymerization for 2 hours at 55°C, the ampoules were opened and the polymers were obtained by precipitating into a large excess of methanol.

Radical Polymerization of GMAPMI

In a glass ampoule, GMAPMI (2.50 g, 7.00 mmol) and AIBN (22.9 mg, 0.14 mmol, 2 mol%) were placed in dioxane (10 ml) and the ampoule were sealed under vacuum. After polymerization for 2 hours at 55°C, the precipitated polymers were collected and dried under vacuum to obtain 1.90 g (76% yield).

The self-polymerization of GMAPMI for 2 hours at 55°C without using a initiator was produced only 0.70 g (28% yield) of polymer. The obtained polymers in both cases were insoluble in organic solvents. IR (KBr), ν (cm^{-1}): 3500 (OH stretching), 1720 (C=O of imide and ester stretching), 1608 (C=C of aromatic stretching), 1279 and 1119 (C-O bending), 830 (CH=CH of maleimide).

Radical Copolymerization of GMAPMI with St, NVP, or MMA

Radical copolymerizations of GMAPMI were performed with equimolar amounts of comonomers. Copolymerizations of GMAPMI (930 mg, 2.58 mmol) with 270 mg (2.58 mmol) of styrene, 285 mg (2.58 mmol) of NVP, or 255 mg (2.58 mmol) of MMA, were carried out using 16.8 mg (0.102 mmol, 2 mol%) of AIBN or without AIBN in dioxane (4.8 ml) for 2 hours at 55°C under argon. The precipitated polymers were collected and dried under vacuum to obtain crosslinked copolymers (Table 1). All of the polymers were insoluble in organic solvents. IR (KBr) of Poly(GMAPMI-co-St) ν (cm^{-1}): 3500 (OH stretching), 1720 (C=O of imide and ester stretching), 1635 (C=CH$_2$ stretch-

TABLE 1. Radical Polymerizations of Bifunctional N-phenylmaleimides[a]

Monomers	M / S[b] (g / ml)	AIBN (mol %)	Yield (%)
GMAPMI (1)	0.25	-	28
GMAPMI (1)	0.25	2	76
1 / NVP	0.25	-	71
1 / NVP	0.25	2	95
1 / Styrene	0.25	-	75
1 / Styrene	0.25	2	95
1 / MMA	0.25	-	22
1 / MMA	0.25	2	75
MAPMI (2)	0.30	-	32
MAPMI (2)	0.30	1	70
MIBOSt (3)	0.30	-	78
MIBOSt (3)	0.30	1	99

[a]Polymerizations were carried out for 2 h at 55 ℃ in dioxane with or without using AIBN as a radical initiator. Equimolar amounts of comonomers were used in copolymerizations of 1.
[b]M/S is the ratio of the weights of combined monomers to the volume of dioxane.

ing), 1608 (C=C of aromatic stretching), 1290 and 1100 (C-O bending), 830 (weak, CH=CH of maleimide). IR (KBr) of Poly(GMAPMI-co-NVP), ν (cm^{-1}): 3500 (OH stretching), 1720 (C=O of imide and ester stretching), 1640 (C=CH$_2$ stretching), 1610 (C=C of aromatic stretching), 1290 and 1100 (C-O bending), 830 (CH=CH of maleimide). IR (KBr) of Poly(GMAPMI-co-MMA), symbol ν (cm^{-1}): 3500 (OH stretching), 1740 (C=O of imide and ester stretching), 1608 (C=C of aromatic stretching), 1290 and 1100 (C-O bending), 830 (CH=CH of maleimide).

Radical Polymerization of MAPMI and MIBOSt

Polymerizations of MAPMI (500 mg, 1.94 mmol) or MIBOSt (400 mg, 1.26 mmol) were carried out using AIBN (1 mol%) or without AIBN in dioxane (1.7 ml) under argon for 2 hours at 55°C. The yields of crosslinked polymers were summarized in Table 1. IR (KBr) of Poly(MAPMI), ν (cm^{-1}): 1720 (C=O of imide and ester stretching), 1608 (C=C of aromatic stretching), 1300 and 1050 (C-O bending), 830 (weak, CH=CH of maleimide). IR (KBr) of poly(MIBOSt), ν (cm^{-1}): 1720 (C=O of imide and ester stretching), 1608 (C=C of aromatic stretching), 1290 and 1100 (C-O bending), 830 (weak, CH=CH of maleimide).

RESULTS AND DISCUSSION

Synthesis of Bifunctional Maleimides

Reaction schemes for the synthesis of three bifunctional *N*-phenyl-maleimide derivatives are described in Figure 1. *N*-[4-(2-hydroxy-3-methacryl-oyloxypropyloxycarbonyl)-phenyl]maleimide, GMAPMI (1) was prepared by an epoxide ring-opening reaction between *N*-(4-carboxyphenyl)maleimide and gly-cidyl methacrylate. The 1H NMR spectrum of **1** showed a singlet peak at 1.93 ppm for methyl protons and two singlet peaks at 6.13 and 5.59 ppm for two olefin protons in the methacrylate group, and a singlet peak at 6.86 ppm for two olefin protons in the maleimide (MI) group. In an IR spectrum of **1**, characteristic absorption bands corresponding to hydroxyl (3500 cm^{-1}), methacrylate (1635 cm^{-1}) and maleimide (830 cm^{-1}) groups were all identified.

N-(4-Methacryloyloxyphenyl)maleimide, MAPMI **(2)** was prepared by reacting *N*-(4-hyroxyphenyl)maleimide with methacryloyl chloride and 4-(4-maleimidobenzoyl-oxy)styrene, MIBOSt **(3)** was prepared by reacting 4-male-imidobenzoyl chloride and 4-hydroxystyrene. The monomers **2** and **3** were obtained in high yields over 80%. ^{1}H NMR spectra of monomers **2** and **3** clear-
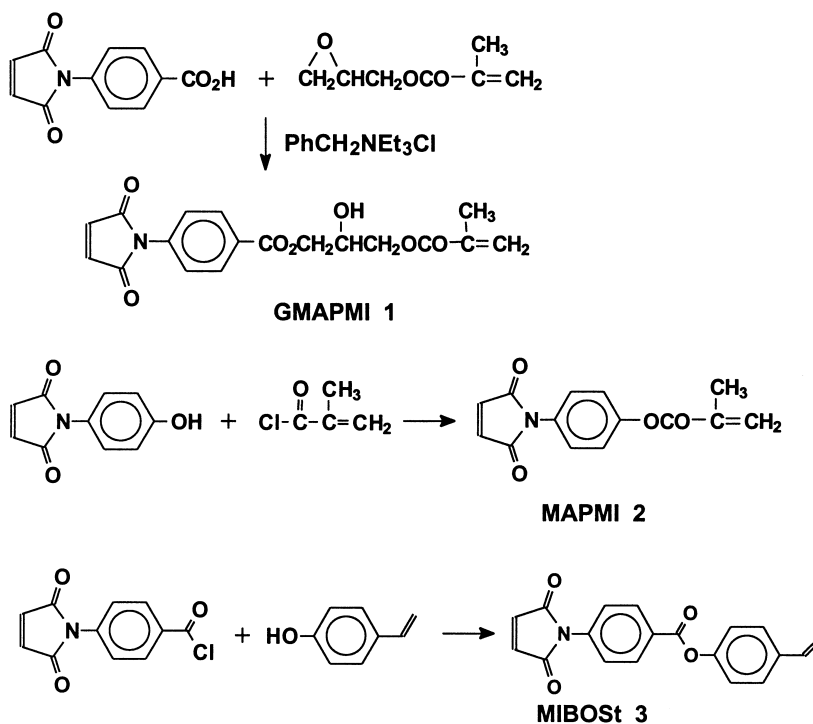
Figure 1. Synthesis of bifunctional N-phenylmaleimide monomers.

ly indicated the presence of methacrylate and styrene functionalities, respectively, along with the maleimide functionality. In the IR spectra, characteristic absorption bands at 1635 cm^{-1} for the methacrylate or the styrene double bond along with the maleimide absorption at 830 cm^{-1} were in accord with the chemical structures of **2** and **3**. The structures of three bifunctional maleimides were also confirmed by ^{13}C NMR spectra and elemental analysis.

Radical Polymerizations

The homo- and copolymerizations of three bifunctional *N*-phenylmaleimde monomers were performed in dioxane solution with or without using AIBN as a radical initiator. The polymerization results are summarized in Table 1. All of the obtained polymers were insoluble in various organic solvents due to the crosslinking of both the polymerizable functionalities. Monomers **1-3** were truly reactive toward the radical initiator to give high polymerization yields when compared with polymerizations without using AIBN. The homopolymerization

yields of the monomer **3** were significantly high, nearly 100% with AIBN and even in the absence of a radical initiator the yield was 78%. The styryl moiety of **3** has higher electron-donor strength than the methacrylate moiety of the comparable monomers **1** and **2**.

The higher polymerizability of the monomer **3** is a strong indication of EDA polymerization even without radical initiators by the well balanced electron donor/acceptor character of two functionalities within the molecule [7, 8]. The homopolymer of GMAPMI, poly(GMAPMI), showed weak absorption bands at 1635 and 830 cm^{-1} in IR spectra indicating the disappearance of double bonds of methacrylate and maleimide moieties, respectively. The chemical structures of those obtained homopolymers of monomer **1-3** were identified by IR spectra as shown in Figure 2. The polymerization progress of the methacrylate and maleimide moieties in the monomer **1** was monitored by determining the decrease in their intensities of absorption bands at 1635 cm^{-1} and 830 cm^{-1} due to the disappearance of the corresponding C=C bonds in the IR spectra. Obviously, the methacrylate groups more rapidly disappeared than the maleimide groups in rad-
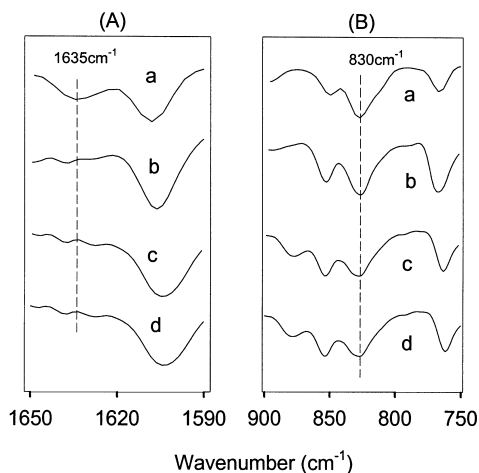

Figure 2. IR spectra of homopolymers of three bifunctional monomers highlighting the characteristic weak absorption bands (A) at 1635 cm^{-1} and 830 cm^{-1} for C=C double bonds of methacrylate and maleimide moiety, respectively: (a) GMAPMI, (b) poly(GMAPMI), (c) poly(MAPMI) and (d) poly(MIBOSt).

ical homopolymerization of **1**, thereby leaving maleimide absorption at 830 cm^{-1} only slightly decreased. In Figure 2(A), the absorption intensities of the methacrylate C=C bonds at 1635 cm^{-1} in three homopolymers appreciably decreased in comparison with the invariable aromatic absorption band at 1610 cm^{-1}. However, in Figure 2(B), the absorption band at 830 cm^{-1} corresponding to the maleimide C=C bonds exhibits a different aspect of copolymerization behaviors between two double bonds in the bifunctional monomers. The homopolymer, poly(GMAPMI), reveals no appreciable change in the region due to the unreacted maleimide moieties (Figure 2B, b), whereas, poly(MIBOSt) shows the significant decrease in the both bands implying the equal participation in the polymerization.

The complex structures of crosslinked poly(GMAPMI) are described in Figure 3. Hence, the polymer chains are supposed to include large amounts of reacted methacrylate units leaving substantial amounts of unreacted maleimide units because of the higher radical polymerizability of the methacrylate units. The predesigned monomers, which have electron donor/acceptor groups simultaneously within the same molecule, are expected to have a strong tendency toward the formation of soluble alternating copolymers by selective EDA polymerization. However, monomer **3** as possessing a balanced EDA character did not secure an ideal alternating polymer structure (perfect ladder shape) as shown in Figure 3 (b). Thus, poly(MIBOSt) was only obtained in a highly crosslinked state.

Radical Copolymerizations of GMAPMI with St, NVP or MMA

To investigate further the reactivities of two functionalities, GMAPMI were copolymerized with various comonomers such as styrene (St), *N*-vinyl-2-pyrrolidinone (NVP) and methyl methacrylate (MMA) and the results are also summarized in Table 1. Electron-donor monomers such as St and NVP resulted in high copolymerization yields because of the high EDA polymerization tendency even without a radical initiator. The copolymerization yields were also much higher when a radical initiator was used. All of the obtained copolymers were again insoluble in various organic solvents. IR spectra confirmed the chemical structures of the copolymers, exhibiting all the absorption bands attributable to the functional groups comprised in the copolymers as shown in Figure 4. In the IR spectra, broad and strong absorption bands corresponding to carbonyl groups appear at around 1730 cm^{-1} for the methacrylate and maleimide groups. Styrene and NVP as an electron-donor were initially copolymerized with the
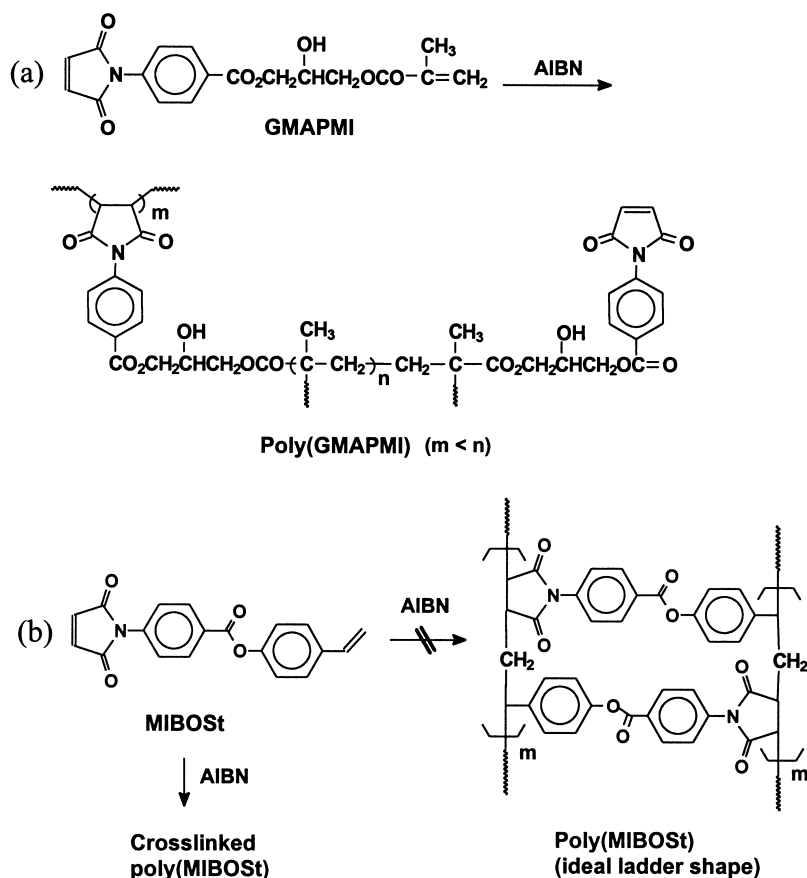
Figure 3. Crosslinked polymer structures obtained by radical homopolymerizations of (a) GMAPMI and (b) MIBOSt with an ideal ladder shape polymer of MIBOSt.

maleimide moiety of **1** as an electron-acceptor evidenced by the pronounced decrease in the absorption intensity at 830 cm^{-1} due to the preferential reaction of maleimide moieties (spectrum b in Figure 4). Copolymerization of **1** with MMA rendered the similar decrease in absorption due to the comparable reaction of both C=C double bonds as shown in a spectrum c of Figure 4. In Figure 4, the absorption intensity at 830 cm^{-1} of the copolymer, poly(GMAPMI-co-NVP), significantly decreased in comparison with poly(GMAPMI) and poly(GMAPMI-co-MMA).
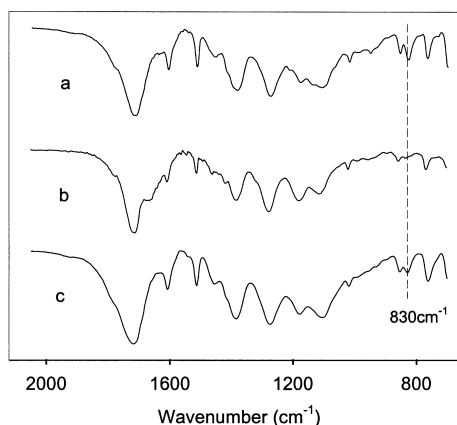
Figure 4. IR spectra of (a) poly(GMAPMI), (b) poly(GMAPMI-co-NVP) and (c) poly(GMAPMI-co-MMA).

In general, 1,2-disubstituted ethylene monomers are less reactive in their free radical polymerizations than mono- or 1,1-disubstituted ethylenes [10]. Indeed, N-phenylmaleimide is known to have very low polymerizability compared with common vinyl monomers but it has much greater copolymerizability by EDA polymerization in an alternating fashion when copolymerized with styrene as an electron-rich monomer [5, 19, 20]. *N*-Phenylmaleimide (as M_1) was copolymerized sluggishly with MMA (as M_2) having monomer reactivity ratios, $r_1 = 0.38$ and $r_2 = 1.20$ as reported in a paper [22]. Therefore, the homopolymerization of the bifunctional GMAPMI could be proceeded by the multiple radical addition to methacrylate moieties with sporadic inclusion of maleimide moieties leaving many of maleimide double bonds intact as described in Figure 3. It is known that methacrylates monomers do not copolymerize well with NVP [23]. For example, the reactivity ratios for the copolymerization of MMA (M_1) and NVP (M_2) are $r_1 = 5$ and $r_2 = 0.02$. NVP and styrene as electron-donating comonomers were readily copolymerized with GMAPMI as an electron-acceptor in high yields over 95%. Thus, the high copolymerization tendency of GMAPMI could be explained by the preferential EDA polymerization between its maleimide moiety and styrene or NVP with or without a radical initiator as envisaged in Figure 5. The methacrylate moieties, then, are copolymerized with the comonomer and others, thereby subsequent crosslinking. MMA did not give
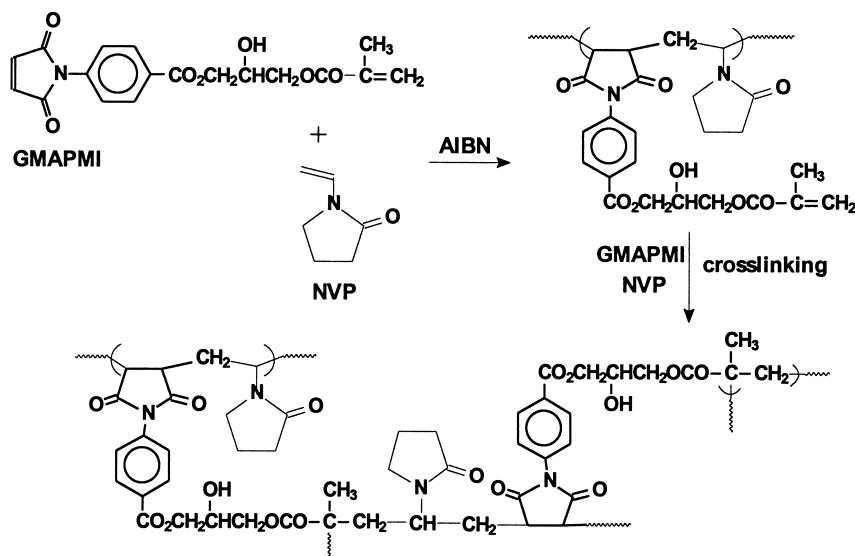
Crosslinked polymers of GMAPMI and NVP

Figure 5. Radical copolymerization of GMAPMI with NVP through preferential EDA polymerization along with copolymerization of methacrylate moieties.

comparable copolymerization yields with GMAPMI because the methacrylate group is not enough as an electron-donor, but it still rendered 75% yield through copolymerization with methacrylates rather than maleimide moieties.

All of the obtained polymers were highly crosslinked, brittle solids and insoluble in organic solvents. The thermal degradation of the obtained polymers observed to begin at about 350°C. Recently, a few reports on photoinduced radical copolymerizations utilizing maleimides and electron-donor monomers in the absence of photoinitiators have gained much attention [8, 23]. We have further explored the photopolymerizations of those bifunctional maleimide monomers and the results will be reported in a subsequent paper [24]. As a beneficial application of such bifunctional monomers, there have been issued interesting insights for recycling thermoset polymers by a thermally reversible Diels-Alder reaction based on the bifunctional styrene monomers containing a furfuryl moiety [4, 25].

CONCLUSION

Three bifunctional *N*-phenylmaleimide monomers containing two different double bonds within the same molecule were prepared and subjected to radical polymerization. The superior reactivity for homopolymerization of monomer **3** with or without radical initiators comes from the balanced electron-donor/acceptor strength between the maleimide and styryl moieties. Comonomers like NVP and styrene as a good electron-donor were readily copolymerized with the maleimide moiety of **1** as a electron-acceptor. The driving force for the homo- and copolymerizations in high yields are ascribable to the electron-donor/acceptor polymerization tendency between the polymerizable double bonds. All of the attempts are undergoing to construct a soluble alternating polymer architecture having a perfect ladder shape by taking advantage of selective EDA polymerization between the electron-donor and acceptor moieties within a single molecule.

ACKNOWLEDGEMENTS

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