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Synthesis and Polymerization of *N*-(4-Vinylphenyl)maleimide

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Introduction

Few monomers that have two polymerizable vinyl groups such as divinylbenzene and methylene dimethacrylate are utilized as cross-linking agents. In these monomers the reactivities of the two vinyl groups are almost the same. Monomers possessing two polymerizable groups of different polymerization reactivities will be able to open a new field for polymer reactions and macromolecular networks. However, it is generally difficult for the monomers with two carbon–carbon double bonds of different reactivities to enable one double bond to be polymerized exclusively, retaining potentiality for polymerization of the other double bond.

N-Substituted maleimides having polymerizable vinylene groups can easily be prepared by the reaction between maleic anhydride and corresponding primary amines.[1,2] Anionic polymerization of N-substituted maleimides shows several interesting features.[2–6] For example, anionic polymerization of *N*-phenylmaleimide (*N*-PMI) exhibits "living" character which leads to poly(*N*-PMI) with the desired molecular weight.[4]

Poly(N-substituted maleimide)s are thermostable,[3] so that poly(maleimide) derivatives with pendant vinyl groups can be polymeric, new thermostable materials which are modifiable through polymer reactions.

The vinylene group of a maleimide moiety reacts easily with a thiol group.[7] This reaction is very important and useful for modification of proteins with a thiol group[7] and determination of L-ascorbic and L-dehydroascorbic acids.[8] A maleimide moiety is also a dienophile in the Diels–Alder reaction.[9] Thus, the polymer with the maleimide moiety has excellent potential for versatile reactivity.

This paper describes the synthesis and polymerization of *N*-(4-vinylphenyl)maleimide (*N*-VPMI), which possesses two polymerizable carbon–carbon double bonds with different reactivities, one of which is the vinylene group of the maleimide moiety and the other the vinyl group of the styrene moiety.

Using this concept we report the preparation of new polymers from *N*-VPMI that have different pendant reactive groups by variation in the initiator used. Polymerization reactions which were expected to proceed with living character[4,10] were used to obtain new materials with a controlled structure.

Experimental Section

All experiments for polymerization reactions were carried out under purified nitrogen atmosphere to exclude oxygen and moisture.

Reagents. 4-Aminophenethyl alcohol and maleic anhydride were used as received. Dichloromethane was purified by treatment with sulfuric acid, dried by refluxing over calcium hydride, and distilled before use. Boron trifluoride etherate was purified by distillation. AIBN was purified by recrystallization from methanol. Lithium *tert*-butoxide, potassium *tert*-butoxide, toluene, and THF were purified in the same way as described in a previous paper.[3] Cesium *tert*-butoxide was synthesized from 2-methyl-2-propanol with cesium metal.

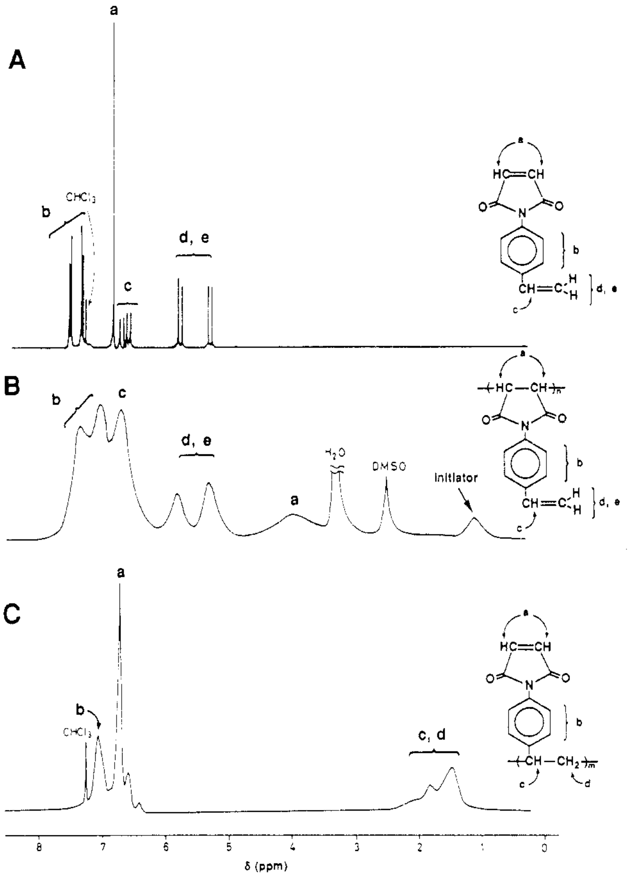

Figure 1. ^{1}H NMR spectra of (A) *N*-VPMI monomer, (B) poly(*N*-VPMI) prepared with *tert*-C_4H_9OK[poly(*N*-VPMI)$_{MI}$ (run 4 in Table I)], and (C) poly(*N*-VPMI) prepared with $BF_3 \cdot O(C_2H_5)_2$-[poly(*N*-VPMI)$_{ST}$ (run 7 in Table I)].

Synthesis of 4-Aminostyrene.[11] A total of 25 g (182 mmol) of 4-aminophenethyl alcohol, 35 g of potassium hydroxide, and 0.25 g of 4-*tert*-butylcatechol were placed in a distillation flask in a sand bath and heated to 200–250 °C under reduced pressure (5–15 mmHg). Distillate was extracted by ether. The ether solution was dried with sodium hydroxide and evaporated. Distillation under reduced pressure [71–76 °C (2 mmHg)] yielded 10.9 g (50.2%) of 4-aminostyrene.

Synthesis of *N*-(4-Vinylphenyl)maleimide (*N*-VPMI). The compound was prepared by a modified method for synthesis of *N*-PMI.[1,2] In a 200-mL three-necked flask provided with a stirrer, a reflux condenser, and a dropping funnel were placed 4.22 g (43 mmol) of maleic anhydride and 60 mL of ethyl ether. A ether solution (20 mL) of 4-aminostyrene (5.12 g, 43 mmol) was added to the flask through the dropping funnel. The resulting suspension was stirred for 1 h at room temperature and then cooled to 10–15 °C in an ice bath. The yellow powder was collected by suction filtration (yield, 8.92 g). To the mixture of 22 mL of acetic anhydride and 2 g of anhydrous sodium acetate was added the powder obtained as above, and the resulting mixture was stirred over a steam bath for 30 min. The reaction mixture was cooled to room temperature and the poured into a large amount of ice water. The product precipitated was collected by suction filtration and washed three times with ice-cold water and once with petroleum ether. Recrystallization from cyclohexane gave yellow needles. Yield: 7.22 g (84.3%). Mp: 104–105 °C. ^{1}H NMR ($CDCl_3$): δ 5.30 (d, J_{cis} = 10.8 Hz, 1 H, C*H*H of vinyl), 5.77 (d, J_{trans} = 16.2 Hz, 1 H, CH*H* of vinyl), 6.73 (dd, J_{cis} = 10.8 Hz, J_{trans} = 16.2 Hz, 1 H, CH of vinyl), 6.84 (s, 2 H, CH of vinylene), 7.32 and 7.49 (m, 4 H, phenyl). See Figure 1A.

^{13}C NMR ($CDCl_3$): δ 115.0 (CH_2, vinyl), 126.0 and 126.8 (CH, phenyl), 130.5 and 137.2 (C, phenyl), 134.2 (CH, vinylene), 135.8 (CH, vinyl), 169.5 (C, carbonyl). IR (KBr, cm^{-1}): ν (C=O

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Table I
Polymerization of N-VPMI[a]

run	initiator	solvent	temp, °C	time, h	yield, %
1	AIBN[b]	THF	60	6	95.2
2	*tert*-C_4H_9OLi	THF	−72	3	1.3
3	*tert*-C_4H_9OK	THF	0	3	68.1
4	*tert*-C_4H_9OK	THF	−72	3	66.0
5	*tert*-C_4H_9OCs	THF	−72	3	70.6
6	$BF_3{\cdot}O(C_2H_5)_2$	DCM[c]	0	3	11.2
7	$BF_3{\cdot}O(C_2H_5)_2$	DCM[c]	0	6	20.6

[a] For ionic polymerization: [N-VPMI] = 2.5×10^{-1} mol/L, [initiator] = 1.0×10^{-2} mol/L. [b] [N-VPMI] = 1.2×10^{-1} mol/L, [AIBN] = 1.6×10^{-3} mol/L. [c] Dichloromethane.

(stretching) of imide) 1717; δ (CH (out-of-plane) of $CH{=}CH_2$) 994 and 911; δ (CH (out-of-plane) of 1,4-disubstituted phenyl) 837. Anal. Calcd for $C_{12}H_9NO_2$: C, 72.35; H, 4.55; N, 7.03. Found: C, 72.51; H, 4.39; N, 7.12.

Polymerization. *N*-VPMI purified by recrystallization was used as a monomer after thoroughly dried below 20 °C under reduced pressure. THF (solvent) and a THF solution of the monomer were placed into an ampule which had been carefully flame dried. Polymerization was started by the addition of a THF solution of initiator to the monomer solution at a determined temperature with stirring. After a definite time, the polymer was isolated by precipitation from a mixture of ether/methanol (3/1 (v/v)), washed with methanol three times, and then dried in vacuo below 20 °C to constant weight. The structure of the resulting poly(*N*-VPMI) was confirmed by ^1H NMR and IR (see the Results and Discussion section).

Measurements. A ^1H NMR spectrum was recorded on a JEOL GSX-270 FT-NMR spectrometer using deuterated dimethyl sulfoxide or chloroform as solvent. An IR spectrum was measured on a JASCO IR-700 spectrometer. GPC was measured with a TOSOH HLC-802A apparatus at 38 °C with TSK gel G40000HXL–G3000HXL–G2000HXL column series using THF as eluent (flow rate 1.0 mL/min). For poly(*N*-VPMI) obtained with an anionic initiator (poly(*N*-VPMI)$_{MI}$), the molecular weight measured by GPC was calculated from the calibration curve corrected for poly(*N*-PMI),[4] and for poly(*N*-VPMI) obtained with a cationic initiator (poly(*N*-VPMI)$_{ST}$), the molecular weight was calculated from the calibration curve for polystyrene.

Results and Discussion

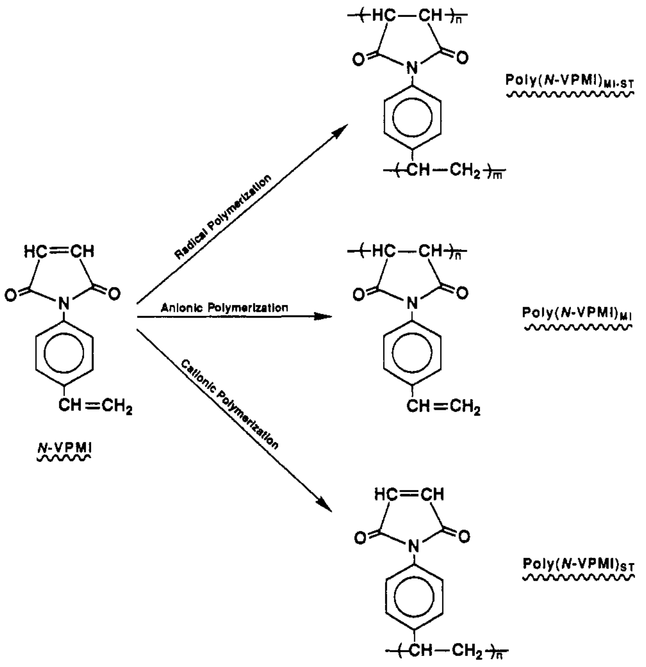
Results of the polymerizations of *N*-VPMI are summarized in Table I. Polymerizations of *N*-VPMI were carried out with radical, anionic, and cationic initiators.

Polymerization with AIBN as a radical initiator gives polymeric materials in 95.2% yield at 60 °C in THF for 6 h. The material produced was a white solid which could not be dissolved in any available organic solvents.

It was previously reported that styrene and N-substituted maleimide were radically copolymerized to form an alternative copolymer in the wide range of the monomer feed ratios. Monomer reactivity ratios were evaluated to be $r_1 = 0.012$ and $r_2 = 0.047$ for styrene (M_1) and *N*-PMI (M_2).[12] In the radical polymerization of *N*-VPMI, both vinyl and vinylene double bonds in the monomer probably incorporated in the reaction to cause gelation. In other words, the polymer produced here should be a cross-linked gel. (see poly(*N*-VPMI)$_{MI\text{-}ST}$ in Scheme I).

With anionic initiators, polymeric materials are also obtained. Alkali-metal *tert*-butoxides produced polymers of *N*-VPMI. Potassium *tert*-butoxide and cesium *tert*-butoxide gave polymers in more than 60% yields. Previous studies revealed that alkali-metal *tert*-butoxides can initiate polymerization of N-substituted maleimides[2,4] but are inactive for anionic polymerization of styrene derivatives,[13] and, further, these polymerizations are influenced by the size of countercation with respect to the polymer yields, as observed for *N*-PMI.[2] Similar results were obtained also in the polymerization of *N*-VPMI, where a 70.6% yield of polymer was obtained with cesium *tert*-butoxide and, in contrast, only 1.3% with lithium *tert*-butoxide in THF for 3 h at −72 °C.

Scheme I



The polymers obtained with the anionic initiators were yellow powder which were soluble in THF, 1,4-dioxane, dimethyl sulfoxide, *N*,*N*-dimethylformamide, and pyridine, while insoluble in chloroform, acetone, ether, alcohol, and hydrocarbon solvents.

The ^1H NMR spectrum of poly(*N*-VPMI) obtained with potassium *tert*-butoxide is shown in Figure 1B. The signal at 6.8 ppm assigned to the vinylene protons of the *N*-VPMI monomer is absent and a new broad signal appears around 4 ppm which is assignable to the methine protons of a poly(N-substituted maleimide) structure.[4] The signal intensity ratios of the vinylene protons to the phenyl protons of the *N*-VPMI monomer in Figure 1A and of the methine protons of poly(*N*-VPMI) to the phenyl protons in Figure 1B are the same (2:4). Signals around 5.3, 5.8, and 6.7 ppm, which are assigned to the vinyl protons of the styrenic moiety, are unchanged with respect to the intensity ratio to the phenyl protons. The signals of the vinyl protons in the spectrum of poly(*N*-VPMI) are broadened, and splits by spin–spin coupling are not observed, due to the low mobility of the poly(*N*-VPMI) molecule. On an IR spectrum of poly(*N*-VPMI), absorptions at 994 and 911 cm^{-1}, which were observed in the case of *N*-VPMI and assigned to the CH out-of-plane deformation vibration of the vinyl group, were unchanged.[14] These spectral data indicate that anionic polymerization with alkali-metal *tert*-butoxide initiators takes place exclusively at the carbon–carbon double bonds of the maleimide moiety in *N*-VPMI. The poly(*N*-VPMI) obtained with alkali-metal *tert*-butoxide initiators, therefore, has a poly(*N*-PMI) main chain with pendant styrenic vinyl groups (poly(*N*-VPMI)$_{MI}$ in Scheme I).

As shown in Figure 2A, the molecular weight distribution of poly(*N*-VPMI)$_{MI}$ obtained with potassium *tert*-butoxide is unimodal and rather broad, which is similar to that of poly(*N*-PMI) produced with the same initiator. Average molecular weights were estimated to be 3.1×10^3 for $\bar{M}_n$ and 3.8×10^3 for $\bar{M}_w$ ($\bar{M}_w/\bar{M}_n = 1.3$) based on a calibration curve for poly(*N*-PMI).[4] The value of the number-average

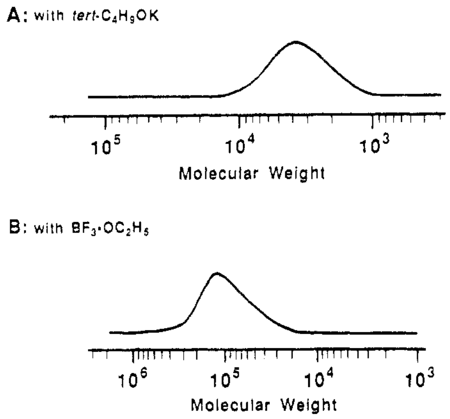


Figure 2. GPC eluograms of (A) poly(*N*-VPMI) prepared with *tert*-C_4H_9OK[poly(*N*-VPMI)$_{MI}$ (run 4 in Table I)] and (B) poly(*N*-VPMI) prepared with $BF_3{\cdot}O(C_2H_5)_2$[poly(*N*-VPMI)$_{ST}$ (run 7 in Table I)].

molecular weight of this polymer is in good agreement with the calculated value (2.9×10^3, from the data of run 4 in Table I) assuming living character of the polymerization.[15]

N-VPMI can also be polymerized under typical cationic polymerization conditions. $BF_3{\cdot}O(C_2H_5)_2$ produces a 20.6% yield of poly(*N*-VPMI) in dichloromethane at 0 °C for 6 h as shown in Table I. It is to be noted that *N*-phenylmaleimide was not polymerized under the same polymerization conditions. An initiator system of HI/$ZnCl_2$,[16] which is reported to initiate living cationic polymerization of substituted styrenes, failed to give a polymer of *N*-VPMI. The polymer obtained (run 7 in Table I) was a slightly yellow powder which was soluble in THF, 1,4-dioxane, chloroform, dichloromethane, acetone, dimethyl sulfoxide, *N,N*-dimethylformamide, and pyridine, while insoluble in ether, alcohol, and hydrocarbon solvents.

The ^1H NMR spectrum of poly(*N*-VPMI) obtained with $BF_3{\cdot}O(C_2H_5)_2$ is shown in Figure 1C. Signals due to the vinyl protons in the *N*-VPMI monomer (around 5.3, 5.8, and 6.7 ppm) are absent, and new broad signals appear in the region from 1.3 to 2.4 ppm which are assignable to the methylene and methine protons of a polystyrene structure.[17] The signal intensity ratio of the vinyl protons of *N*-VPMI to the phenyl protons in Figure 1A and that of the methylene and methine protons of poly(*N*-VPMI) to the phenyl protons in Figure 1C are the same (3:4). A signal at 6.8 ppm, assigned to the vinylene protons, is unchanged with respect to the intensity ratio to the phenyl protons. The signal is broadened, and splits by spin–spin coupling are not observed in the spectrum of the poly(*N*-VPMI) by the same reason as for the polymer obtained with potassium *tert*-butoxide as an initiator. For an IR spectrum of poly(*N*-VPMI), absorptions of the vinyl group (994 and 911 cm^{-1}) disappeared. These results indicate that cationic polymerization with $BF_3{\cdot}O(C_2H_5)_2$ takes place not at the vinylene group but only at the vinyl group of the *N*-VPMI monomer. Thus, it is concluded that poly(*N*-VPMI) obtained with $BF_3{\cdot}O(C_2H_5)_2$ has a polystyrene main chain with pendant maleimide moieties and vinylene groups (poly(*N*-VPMI)$_{ST}$ in Scheme I).

The GPC eluogram, given in Figure 2B, shows that the molecular weight distribution of poly(*N*-VPMI)$_{ST}$ with $BF_3{\cdot}O(C_2H_5)_2$ is unimodal, and average molecular weights were estimated to be 8.2×10^4 for $\bar{M}_n$ and 1.2×10^5 for $\bar{M}_w$ ($\bar{M}_w/\bar{M}_n = 1.5$) based on a calibration curve for polystyrene.

Poly(*N*-VPMI)$_{MI}$ and poly(*N*-VPMI)$_{ST}$, both of which possess the polymerizable carbon–carbon double bonds as pendant groups, formed insoluble gels when they were subjected to radical polymerization by heating or treating with AIBN.

In conclusion, by choosing ionic polymerization methods, either of the two different polymerizable groups (vinylene of the maleimide type and vinyl of the styrene type) of *N*-VPMI can be polymerized exclusively to give poly(*N*-PMI) with pendant vinyl groups and polystyrene with pendant maleimide moieties without cross-linking, whereas radical polymerization gave only an insoluble gel.

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(14) For vinyl and vinylene groups, assignments of absorptions of the C=C stretching in *N*-VPMI observed between 1600 and 1700 cm^{-1} failed, because those absorptions overlapped with a very strong and broad absorption of the C=O stretching of the cyclic imide moiety, and, further, the absorption from the phenyl ring is to appear in the same region.

(15) This result is similar to that of anionic polymerization of *N*-PMI with the same initiator, which proceeds with "living" character (see ref 4).

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Registry No. *N*-VPMI (homopolymer), 137028-53-6.