

Synthesis of Heat- and Solvent-Resistant Polymers by Radical Polymerization of Trifluoromethyl-Substituted *N*-Phenylmaleimides

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ABSTRACT: The radical polymerization of the three kinds of fluorine-containing maleimides, that is, *N*-[2-(trifluoromethyl)phenyl]maleimide (2TFPhMI), *N*-[3-(trifluoromethyl)phenyl]maleimide (3TFPhMI), and *N*-[4-(trifluoromethyl)phenyl]maleimide (4TFPhMI) was carried out in the presence of a radical initiator in benzene at 60°C. The polymerization reactivity of these fluorine-containing maleimides and the properties of the resulting polymers were examined in comparison with the results for the methyl-substituted phenylmaleimides. The trifluoromethyl-substituted maleimides readily polymerized to give polymers in high yields as well as a methyl-substituted one. The resulting polymers showed an excellent resistance against organic solvents; especially, poly(4TFPhMI) was insoluble in the most common solvents. The onset temperature of thermal decomposition of the fluorine-containing polymers ($T_{\text{init}} = 352\text{--}368^\circ\text{C}$) was similar to that of poly(*N*-phenylmaleimide) ($T_{\text{init}} = 364^\circ\text{C}$) and slightly lower than those for the methyl-substituted one ($T_{\text{init}} = 388\text{--}402^\circ\text{C}$). The glass transition temperature of the polymers was dependent on the position of the trifluoromethyl group. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 68: 1703–1708, 1998

Key words: radical polymerization; fluorine-containing monomer; *N*-phenylmaleimide; solubility; thermal property; decomposition temperature; glass transition temperature

INTRODUCTION

The polymerization and copolymerization of maleimide derivatives have been studied and the properties of the polymers produced have also been characterized because of their excellent thermal stability.^{1–5} Polymaleimides are prepared through vinyl polymerization, that is, radical or anionic polymerizations, and are strongly ex-

pected to be applied as a new transparent material because of their characteristics different from those of conventional polyimides prepared by condensation polymerization.^{6–10} Previously, Matsumoto et al.⁴ demonstrated that the solubility of poly(*N*-phenylmaleimide) [poly(PhMI)] was modified by the introduction of alkyl groups into the *N*-phenyl ring, especially the substitution of 2,6-positions. Simultaneously, it was also revealed that the polymerization and copolymerization reactivities of the substituted PhMIs depended on the position, number, and bulkiness of the alkyl substituents. For example, the *ortho*-substitution decreased the yield and molecular

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weight of the polymers by steric hindrance in propagation. It was found that the alkyl-substituted poly(PhMI)s were soluble in many kinds of common organic solvents including benzene, chloroform, and tetrahydrofuran and that they showed an excellent thermal stability as well as unsubstituted poly(PhMI). We had an interest in the polymerization reactivity of fluorine-substituted maleimides and the property of the resulting polymers, because fluorine substitution would be expected to gain resistance against organic solvents, as commonly observed for fluoropolymers, and the introduction of fluorine may also change the reactivity of monomers owing to unique properties of an electron negative fluorine.^{11,12}

Some maleimides containing fluorine have been prepared and polymerized by several workers.^{13–21} For example, Barrales-Rienda et al.^{13,14} reported the polymerization of seven kinds of fluoro-substituted PhMIs, that is, 2-fluoro-, 3-fluoro-, 4-fluoro-, 2,4-difluoro-, 2,5-difluoro-, 2,3,5,6-tetrafluoro-, and pentafluoro-PhMIs. They carried out radical and anionic polymerization of these maleimides in bulk or in solution as well as by γ -ray irradiation polymerization. The structure and thermal degradation of the resulting polymers were examined in detail. Recently, Nagai and Takahashi^{15,16} also reported the polymerization behavior of several fluorophenylmaleimides monitored by differential scanning calorimetry. Oishi et al.¹⁷ studied the polymerization of maleimides containing perfluoroalkyl groups in the *N*-substituent. Hagiwara et al.¹⁸ reported anionic polymerizations of pentafluoro-PhMI with several kinds of initiators. Matsumoto et al.⁴ already referred to the polymerization reactivity of *N*-[3-(trifluoromethyl)phenyl]maleimides (3TFPhMI) in radical polymerization and some properties of the resulting polymer.

In this article, we deal with the radical polymerization of three kinds of *N*-[(trifluoromethyl)phenyl]maleimides (TFPhMIs), that is, *N*-[2-(trifluoromethyl)phenyl]maleimide (2TFPhMI), 3TFPhMI, and *N*-[4-(trifluoromethyl)phenyl]maleimide (4TFPhMI). The polymerization reactivity as well as the solubility and thermal properties of the resulting polymers are compared with the results for the methyl-substituted derivatives (MPHMI)s, that is, *N*-(2-methylphenyl)maleimide (2MPhMI), *N*-(3-methylphenyl)maleimides (3MPhMI), and *N*-(4-methylphenyl)maleimide (4MPhMI), as shown in Figure 1.

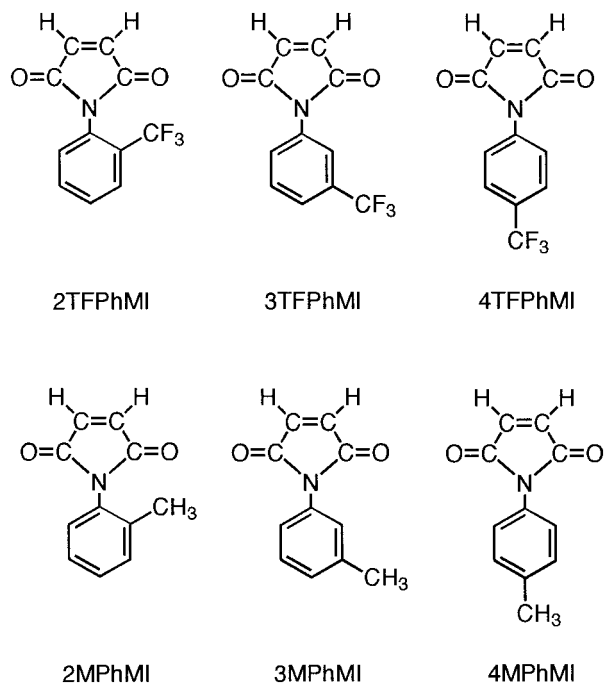


Figure 1 Structure of trifluoromethyl- and methyl-substituted *N*-phenylmaleimides.

EXPERIMENTAL

Materials

TFPhMIs were prepared from maleic anhydride and the corresponding aniline by literature methods.²² Trifluoromethylaniline and maleic anhydride in diethyl ether were stirred at room temperature for 8–12 h. The reaction proceeded slowly and, consequently, the resulting maleamic acid was precipitated. The precipitant was filtered off and dried *in vacuo*. The maleamic acid was allowed to react with acetic anhydride in the presence of sodium acetate at 90°C for 2 h. The structure of the monomers obtained was checked by NMR spectroscopy.

2TFPhMI: Yield 70%. Mp 118.5–119.5°C. ¹H-NMR (60 MHz, CDCl₃) δ 7.3–7.7 (m, aromatic, 4H), 6.71 (s, CH=, 2H). 3TFPhMI (ref. 4): mp 67.0–68.0°C. ¹H-NMR (60 MHz, CDCl₃) δ 7.3–7.7 (m, aromatic, 4H), 6.68 (s, CH=, 2H). 4TFPhMI: Yield 65%. Mp 147.0–149.0°C. ¹H-NMR (60 MHz, CDCl₃) δ 7.0–7.8 (m, aromatic, 4H), 6.71 (s, CH=, 2H).

Dimethyl 2,2'-azobisisobutyrate (MAIB) and 2,2'-azobisisobutyronitrile (AIBN) were recrystallized from ethanol.

Table I Radical Polymerization of TFPhMIs in Benzene at 60°C

| Monomer (mol/L) | Initiator (mol/L) | Time (h) | Yield (%) |
|-----------------|-----------------------------|----------|-----------|
| 2TFPhMI (0.5) | MAIB (5×10^{-3}) | 5 | 42.6 |
| 2TFPhMI (0.5) | AIBN (5×10^{-3}) | 5 | 26.1 |
| 3TFPhMI (0.5) | MAIB (5×10^{-3}) | 5 | 88.9 |
| 4TFPhMI (0.5) | MAIB (5×10^{-3}) | 5 | 71.3 |

Polymerization Procedure

TFPhMI, an initiator, and benzene were placed in a glass ampule. The solution was degassed by the freeze–thaw technique, and then the ampule was sealed *in vacuo*. After polymerization at 60°C for a given time, the polymerization mixture was poured into a large amount of methanol to precipitate the resulting polymer. The yield of the polymer was determined gravimetrically. Benzene should be used very carefully because of its carcinogenicity. Toluene can be also used as the solvent for this polymerization and it is recommended for the reproduction of this work.

Measurements

$^1\text{H-NMR}$ spectra were recorded on a JASCO A202 spectrometer. Differential scanning calorimetry and thermogravimetric analysis were performed in a nitrogen stream at a scanning rate of 10°C/min using a Seiko DSC-200 and TG-200, respectively.

RESULTS AND DISCUSSION

Polymerization Reactivity

The polymerization of TFPhMIs was carried out in the presence of a radical initiator in benzene at 60°C. All the polymerizations of TFPhMIs proceeded inhomogeneously because of the insolubility of the resulting polymers. The polymerization of 2TFPhMI gave the polymer in a lower yield compared with those of 3TFPhMI and 4TFPhMI, as shown in Table I. Figures 2 and 3 show the time–conversion relationship for the polymerization of TFPhMIs. The results of the polymerization of MPhMIs under similar conditions are also included in Figure 3 as the reference.²⁰

The polymerization rate was reduced in the or-

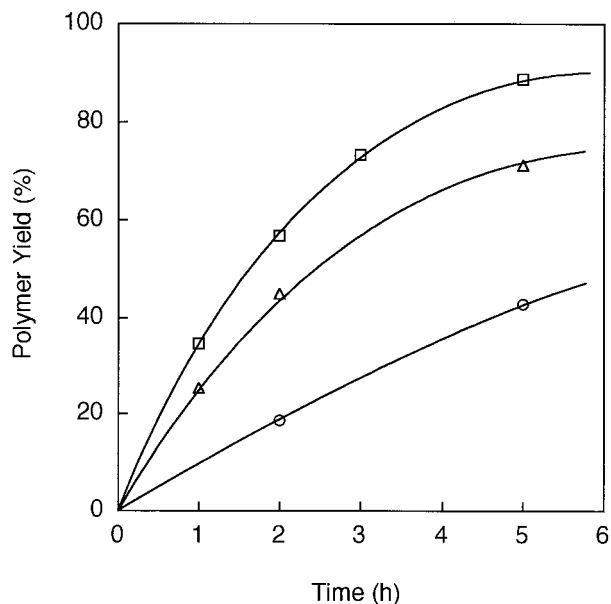


Figure 2 Time–conversion relationship for radical polymerization of TFPhMIs in benzene at 60°C with MAIB: (○) 2TFPhMI; (□) 3TFPhMI; (△) 4TFPhMI. [Monomer] = 0.5 mol/L; [MAIB] = 5×10^{-3} mol/L.

der of the *meta*-, *para*-, and *ortho*-substitution in the series of TFPhMIs and MPhMIs, respectively. The lower polymerization reactivity of *ortho*-substituted PhMIs was already discussed in the pre-

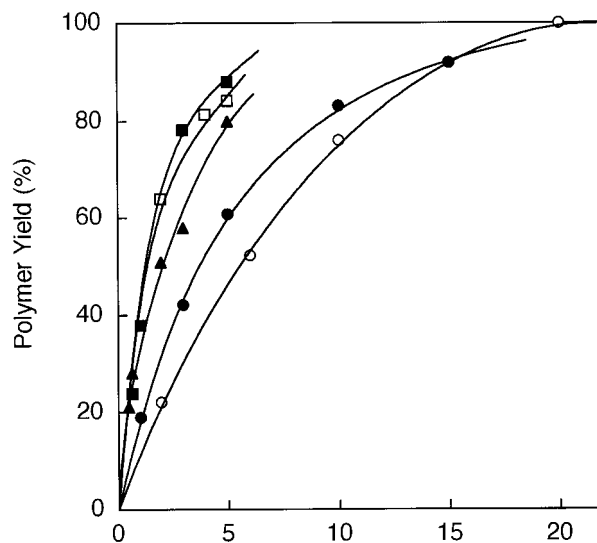


Figure 3 Time–conversion relationship for radical polymerization of TFPhMIs and MPhMIs in benzene at 60°C with MAIB: (○) 2TFPhMI; (□) 3TFPhMI; (●) 2MPhMI; (■) 3MPhMI; (▲) 4MPhMI. [Monomer] = 1.0 mol/L; [MAIB] = 5×10^{-3} mol/L.

Table II Solubility of Poly(TFPhMI)s

| Solvent ^a | Substituent | | |
|-----------------------------|-------------------|-------------------|-------------------|
| | 2-CF ₃ | 3-CF ₃ | 4-CF ₃ |
| Carbon tetrachloride (8.6) | i | i | i |
| Tetrahydrofuran (9.1) | i | i | i |
| Trichloroethylene (9.2) | i | i | i |
| Benzene (9.2) | i | i | i |
| 2-Butanone (9.3) | i | i | i |
| Chloroform (9.3) | i | i | i |
| Anisole (9.5) | i | i | i |
| 1,1,2-Trichloroethane (9.6) | i | i | i |
| Cyclohexanone (9.9) | sw | sw | i |
| 1,2-Dichlorobenzene (10.0) | s | s | sw |
| 1,4-Dioxane (10.0) | i | i | i |
| Acetonitrile (11.9) | i | i | i |
| Dimethyl sulfoxide (12.0) | s | sw | i |
| Dimethylformamide (12.1) | s | sw | i |

s, soluble; sw, swelling; i, insoluble.

^a The values in parentheses indicate a solubility parameter, (cal/cm³)^{1/2}.

vious articles. For example, 2MPhMI polymerizes at a lower rate to provide the polymer with a lower molecular weight compared with 3MPhMI and 4MPhMI because of the suppressed propagation by steric hindrance in both the monomer and the propagating radical.^{4,23} The PhMI with 2-alkoxycarbonyl substituents also showed similar polymerization behaviors.^{24,25} The slightly higher reactivity of 3TFPhMI than of 4TFPhMI, as seen in Table I and Figure 2, is interpreted as an electronic effect; namely, a *para*-trifluoromethyl group is a stronger electron-withdrawing group than that in the *meta* position.

The polymerization rates of TFPhMI and MPhMI bearing the substituents at the same position were as follows: TFPhMI < MPhMI. In the polymerization of the substituted PhMIs, the introduction of an electron-donating group into the *N*-phenyl ring enhances the polymerization reactivity, which is deduced from the polymerization rate and the molecular weight of the polymer, when the steric hindrance is not significant. In contrast to it, an electron-withdrawing group decreases the polymerization reactivity.⁴

The use of AIBN instead of MAIB resulted in the decrease in the polymer yield, while AIBN is the most popularly used azo-initiator for radical polymerization in an organic medium. This is because of less reactivity of the primary radical from AIBN, the 2-cyano-2-propyl radical, toward

2TFPhMI, as previously demonstrated in the polymerization of 2MPhMI²³ and other less reactive vinyl monomers.^{26,27}

Solubility of Polymers

In Table II, the solubility of poly(TFPhMI)s toward a variety of organic solvents is shown. All poly(TFPhMI)s were insoluble in carbon tetrachloride, tetrahydrofuran, trichloroethylene, benzene, 2-butanone, chloroform, anisole, 1,4-dioxane, and acetonitrile. Poly(2TFPhMI) and poly(3TFPhMI) were soluble or swelled in cyclohexanone, 1,2-dichlorobenzene, dimethyl sulfoxide, and dimethylformamide, while poly(4TFPhMI) was swelled in 1,2-dichlorobenzene, but insoluble in the other solvents shown in Table II. Poly(MPhMI)s are soluble in many kinds of organic solvents including nonpolar solvents,⁴ and poly[(*N*-ethoxycarbonylphenyl)maleimide]s are also soluble in several kinds of solvents.²⁴ The high resistance of poly(TFPhMI)s to solvents is due to the strong polar nature of the trifluoromethyl group.

Thermal Properties

The initial decomposition temperature (T_{init}) and the maximum decomposition temperature (T_{max}) were determined by thermogravimetric analysis in a nitrogen stream at a heating rate of 10°C/min. The decomposition temperatures determined are summarized in Table III, together with the previous results for poly(MPhMI)s.⁴

It has been revealed that poly(TFPhMI)s have an excellent thermal stability as well as do the

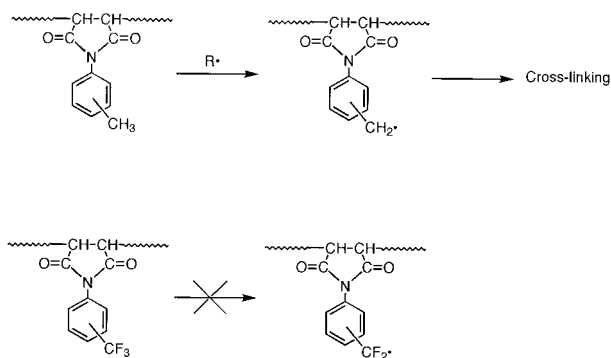
Table III Thermal Properties of Poly(TFPhMI)s

| Polymer | T_{init} (°C) | T_{max} (°C) | T_g (°C) |
|---------------|---------------------------|--------------------------|----------------|
| Poly(2TFPhMI) | 368 | 434 | 328 |
| Poly(3TFPhMI) | 369 ^a | 427 ^a | 339 |
| Poly(4TFPhMI) | 364 | 439 | — ^b |
| Poly(PhMI) | 364 ^a | 422 ^a | — ^b |
| Poly(2MPhMI) | 392 ^a | 427 ^a | 335 |
| Poly(3MPhMI) | 388 ^a | 418 ^a | — ^c |
| Poly(4MPhMI) | 402 ^a | 422 ^a | — ^b |

^a Ref. 4.

^b T_g was not observed below T_{init} .

^c Not determined.



Scheme 1

other polymaleimides.^{4,5} The T_{init} for poly(TFPhMI)s were 364–369°C, being similar to that for poly(PhMI) ($T_{\text{init}} = 364^\circ\text{C}$) and lower than 388–402°C for poly(MPhMI)s, whereas the T_{max} for poly(TFPhMI)s (427–439°C) were slightly higher than those for poly(PhMI) and poly(MPhMI)s (418–427°C). These results are interpreted by the following mechanism (Scheme 1): In the decomposition of poly(MPhMI)s, the abstraction of the hydrogen of the methyl group on the *N*-phenyl ring results in the formation of a benzyl radical. The crosslinked structure produced by the coupling of the radicals would increase the T_{init} value of the polymer. In fact, it has been demonstrated that poly(2MPhMI) yields a partly insoluble fraction after isothermal heating at 360°C.⁴ Contrarily, in the decomposition of poly(TFPhMI)s, such an abstraction and the subsequent crosslinking hardly occur on account of the large energy for the homolytic cleavage of the C—F bond. As a result, the T_{init} 's for poly(TFPhMI)s are same as that of poly(PhMI) and lower than those for poly(MPhMI)s.

The glass transition temperature (T_g) of poly(TFPhMI)s were similar to those of poly(MPhMI)s. The T_g values were 328 and 339°C for the *ortho*- and *meta*-substituted poly(TFPhMI)s, respectively, and 335°C for poly(2MPhMI), while the *para*-substituted polymers did not show a T_g below their decomposition temperatures.

CONCLUSIONS

The radical polymerization reactivity of TFPhMIs were as follows: 3TFPhMI > 4TFPhMI > 2TFPhMI, being similar to the order for the methyl-substituted PhMIs. The poly(TFPhMI)s showed excellent solvent and heat resistance. The T_{init} and T_{max}

values were 352–368°C and 427–439°C, respectively, for poly(TFPhMI)s. The T_g values were 328 and 339°C for poly(2TFPhMI) and poly(3TFPhMI), while poly(4TFPhMI) did not show any T_g below its T_{init} . Thus, we have demonstrated that the polymers of trifluoromethyl-substituted *N*-phenylmaleimides show high onset temperatures of thermal decomposition and high glass transition temperatures, as well as excellent resistance against organic solvents. In the aspect of the practical processing of polymers, the 2-trifluoromethyl-substituted polymer soluble in several organic solvents would be favored rather than the 4-substituted one, which is insoluble in any solvent and does not melt below the decomposition temperature. The copolymerization of these maleimides with vinyl monomers would provide new copolymers with good heat and solvent resistance.

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