Studies of Novel Copolymers for Deep-UV Photoresists. I. Synthesis and Properties of Poly(styrene-*co*-silicon-containing maleimide)

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ABSTRACT: Soluble copolymers of a series of (*N*-maleimido phenoxy) silane monomers with styrene (St) were synthesized by radical polymerization in toluene using 2,2′-azobisisobutyronitrile as initiator. The comonomer reactivity ratios were calculated by the conventional Fineman–Ross and Kelen–Tüdos methods and a nonlinear least-squares Tidwell–Mortimer method. The glass transition temperatures (T_g's) and thermal degradation of copolymers were determined by differential scanning calorimetric and thermogravimetric analysis methods respectively. The introduction of silane side-chain into maleimide (MI) monomers changed the comonomer reactivity ratio with styrene from an alternating to azeotropic copolymerization. The curves of T_g's versus the different compositions of the synthesized St-MI copolymers (mentioned earlier) matched a modified Johnston's equation as increasing the effect of weight ratio on alternating segment, and exhibited an S-shaped curve of deviation in comparison with the Fox's equation. The MI segments within these copolymers exhibited a good compatibility, and the thermal stability and flame retardancy of polystyrene could be enhanced simultaneously via the introduction of silicon-containing MI. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 3369–3375, 2006

Key words: poly(styrene-*co*-maleimide); copolymerization; reactivity ratio

INTRODUCTION

Maleimide (MI) polymers have good thermal stability with high glass transition temperature (T_g) because of their polar five-membered imide ring structure. The functional polymaleimides made from various functionalized MI monomers also provide some desirable properties. Up to now, applications of *N*-substituted MI polymers include photo-resist with high T_g,[1,2] flexibilizer for thermosetting polymers,[3–6] nonlinear polymer with high T_g and flame retardancy,[7] etc. Some *N*-protected polymaleimides have been investigated for their applicability as thermally stable resist materials in the deep ultraviolet region based on the chemical amplification concept.[8–11] The photoresist film should possess high resolution, high sensitivity, high etching resistance, good thermal stability, and high adhesion for the lithographic processes. Incorporating silicon in the polymaleimide structure could advantageously provide good dry-etch resistance and enhanced adhesion to substrates.[12,13]

N-aryl maleimide (AM) monomers, such as *N*-phenyl maleimide (PM), *N*-hydroxyphenyl maleimide (HPM), and halide-substituted *N*-hydroxyphenyl maleimide (XHPM), were usually copolymerized with ethylene or propylene series monomers to promote their heat and fire resistance. Many researches on the AM copolymers, such as the copolymers with styrene,[14–16] methyl methacrylate,[17–19] acrylonitrile,[20] or vinyl acetate,[21] have been reported so far.

These copolymers synthesized by introducing the rigid and high thermal stability of AM segment own higher softening points (or T_g) and good fire resistance. Comparing the double bonds of AM and styrene comonomers with poor-electron and rich-electron density, respectively, a nearly complete alternating copolymer can be formed by free radical copolymerization. The copolymerization behavior of truly alternating styrene–maleic-anhydride copolymer has already been reported by many researchers.[22–25] But, the silicon-containing AM systems are still rarely mentioned in literature.

Our team has already designed a series of different silicon-containing side chains introducing into AMs with high thermal stability, which could be polymerized by free radical initiator to form the soluble homopolymer.[26] In this article we discuss the reactivity ratios of four styrene/silicon-containing AM pairs in copolymerization to study their copolymerized behaviors. The T_g's and thermal stabilities of the synthesized copolymers are also discussed. The possibility of these

copolymers to be used as photoresist materials will then be confirmed furthermore.

EXPERIMENTAL

Materials

Styrene (St), obtained from TCI (Tokyo, Japan), was distilled under reduced pressure after removal of the inhibitor by the usual method and kept cold until further use. Trimethyl(4-(N-maleimido) phenoxy) silane (TMMS), triphenyl(4-(N-maleimido) phenoxy) silane (TPMS), t-butyldimethyl(4-(N-maleimido) phenoxy) silane (BMMS), and triethyl(4-(N-maleimido) phenoxy) silane (TEMS) were prepared by the method described in our previous paper.[26] The synthesized products were dissolved in ethyl acetate and extracted by a 1% NaOH solution. The organic layer was isolated and the remains, dried with anhydrous magnesium sulfate, were then dissolved in ethyl acetate and recrystallized several times with n-hexane. The silicon-containing MI monomers obtained were dried in vacuum. The characterization of this monomer synthesized was analyzed by the ^{1}H, ^{13}C, ^{29}Si nuclear magnetic resonance (NMR) spectroscopy, Fourier transform infrared reflection (FTIR) spectroscopy, and elemental analysis.

The initiator, 2,2′-azobisisobutyronitrile (AIBN), was recrystallized from ethanol and dried in a desiccator. Its melting point, analyzed by DSC, was found to be 104.1°C. Tetrahydrofuran (THF) was distilled after dehydration with sodium. N,N-Dimethylformamide was dried by CaH$_2$ overnight. The other solvents were purified by conventional methods.

Synthesis of copolymer

A flask was charged with various ratios of styrene and MI monomers obtained as shown in Table I, AIBN as initiator (5 mmol/L) and toluene as solvent. The free radical copolymerization was carried out in a water bath thermostat at 70°C and the mixture was refluxed for a time in which the conversion of copolymerization was restricted to less than 10% to satisfy the differential copolymerization equation.[27] The solvent was removed under reduced pressure, and then the polymerization mixture was again dissolved in dichlorome-

TABLE I
Properties of Copolymers Prepared from Styrene (M$_1$) and
Silicon-Containing MI (M$_2$) Monomers

Monomer (M$_2$)	F_2[a]	Conversion (%)	f_2[a]	$\overline{M_w}$[b] (10^4)	$\overline{M_n}$[b] (10^4)	$\overline{M_w}/\overline{M_n}$
TPMS	0.90	9.7	0.86	22.1	6.3	3.51
	0.75	9.2	0.72	23.4	6.8	3.44
	0.60	9.0	0.58	24.2	7.2	3.36
	0.50	9.5	0.49	24.6	7.4	3.32
	0.40	8.6	0.46	25.2	7.7	3.27
	0.25	7.8	0.31	26.2	8.2	3.19
	0.10	8.2	0.20	26.4	8.5	3.11
BMMS	0.90	7.1	0.85	23.9	6.9	3.47
	0.75	8.4	0.71	24.9	7.3	3.41
	0.60	8.8	0.58	25.6	7.7	3.33
	0.50	9.2	0.48	25.9	7.9	3.28
	0.40	7.9	0.45	26.5	8.2	3.23
	0.25	8.9	0.30	27.1	8.6	3.15
	0.10	9.0	0.16	27.4	8.9	3.08
TEMS	0.90	8.1	0.84	24.4	7.1	3.44
	0.75	8.9	0.70	25.5	7.5	3.40
	0.60	8.2	0.57	26.6	8.0	3.33
	0.50	9.2	0.47	27.1	8.3	3.26
	0.40	8.6	0.44	27.2	8.5	3.20
	0.25	8.8	0.30	27.8	8.9	3.12
	0.10	9.5	0.15	28.1	9.2	3.05
TMMS	0.90	9.1	0.82	24.6	7.2	3.42
	0.75	9.4	0.69	25.7	7.6	3.38
	0.60	8.9	0.56	26.9	8.1	3.32
	0.50	9.0	0.46	27.3	8.4	3.25
	0.40	7.6	0.43	27.6	8.6	3.21
	0.25	8.8	0.29	28.6	9.1	3.15
	0.10	9.2	0.14	28.7	9.5	3.02

[a] F_2 and f_2 are the mole fractions of M$_2$ in the feed and in the copolymers while f_2 are obtained from element analysis.
[b] Distribution of molecular weight is tested by GPC with a concentration of 0.5 wt % in THF.

thane and poured into a large amount of methanol. The copolymer then was isolated by filtration and dried under vacuum at 60°C.

Instrumentation

The IR spectra, ^{13}C- and ^{1}H NMR spectra, and elemental analyses (C, H, N) of the St-MI copolymers were obtained by a Nicolet Omnic 3 FTIR spectroscopy, Bruker MSL NMR spectrometer and a Heraeus CHN-O rapid analyzer, respectively. The molecular weight distributions of the St-MI copolymers were measured by a Waters gel permeation chromatography (GPC, Waters 1515HPLC/2410RI-detector) at a flow rate of 1.0 mL/min, with a sample concentration of 0.5 wt % in THF as effluent flow. The system was first calibrated using standard samples of polystyrene with the narrow distribution of molecular weight. The thermal properties of the synthesized copolymers were investigated by DSC (TA-Instruments DSC 10) at a heating rate of 10°C/min under N_2, and TGA (TA-Instruments TGA 51) at a heating rate of 20°C/min under air or N_2, respectively.

RESULTS AND DISCUSSION

Copolymerization and copolymer properties

The copolymers of styrene with silicon-containing PM-series were synthesized by radical polymerization in toluene solution using AIBN as initiator, as shown in Scheme 1.

The FTIR spectra of St/TMMS (50%), St/TPMS (50%), and St/BMMS (50%) copolymers, as shown in Figure 1, revealed the absorption bands (ν) 1240 cm^{-1} (Si—CH$_3$), 1080 cm^{-1} (—Si—O), and 1706 cm^{-1} (C=O) from TMMS; 1430 cm^{-1} (Si—C$_6$H$_5$) from TPMS; 1350 cm^{-1} (—C(CH$_3$)$_3$) from BMMS; and 700 cm^{-1} (monosubstitution of benzene) from styrene. Besides, the chemical shift (δ) of —CH— within styrene unit in
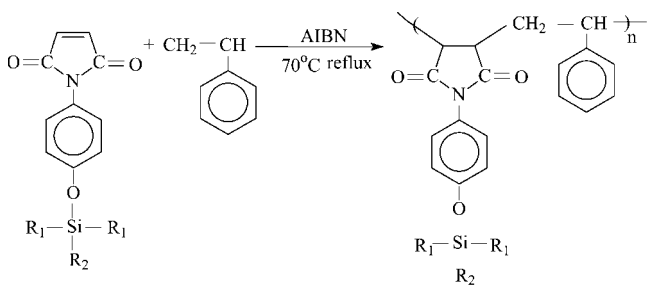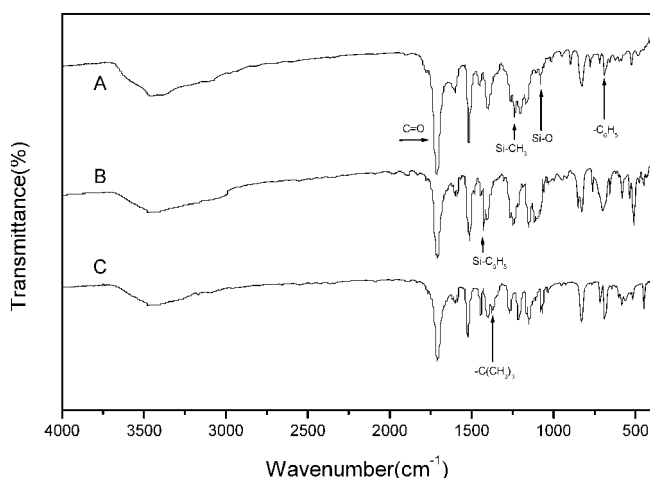

Figure 1 The FTIR spectra of (A) St/TMMS (50%), (B) St/TPMS (50%), and (C) St/BMMS (50%) copolymers.

St/TMMS copolymer measured from ^{13}C NMR and ^{1}H NMR (d-chloroform) appear at about 40.1 ppm and 3.5 ppm, also conforming that these copolymers had been synthesized successfully.

Basic properties of St-MI copolymers in different silicon contents and molecular weights obtained from elemental analysis and GPC analysis are given in Table I. The average number molecular weights $\overline{M_n}$ of each copolymer series were approximately in the range (6.3–9.5) $\times$ 10^4 (g/mol). The $\overline{M_n}$ gradually decreased, while the distribution index of molecular weight increased along with the increasing MI monomers in feed. This might be because the silicon-containing MI monomer could easily cause the chain transfer during copolymerization reaction. Besides, the copolymerization degree and average molecular weight might be affected by the side-chain effect and steric hindrance generated from MI segments. The sequence of intermolecular steric hindrance should be TPMS > BMMS > TEMS > TMMS. Also, since St/TPMS series copolymers would form a larger steric hindrance during copolymerization because of TPMS monomers, a lower polymerization degree and a lower average molecular weight would be obtained.

Generally speaking, the double bond of PM as a result of the electron-withdrawing effect between carbonyl groups on both sides showed its reversed polarity versus styrene monomers.[28] This means that the unsaturated double bonds of PM will be in a poor-electron state and of styrene in a relatively rich-electron state. Then, there was a high tendency for these to copolymerize to generate alternating-like St-MI copolymers with the reactivity ratios approaching 0. The reactivity ratios of styrene/MI comonomers, as shown in Table II, were determined by the method of Fineman–Ross,[29] Kelen–Tüdos,[30] and Tidwell–Mortimer[31] while all the instantaneous copolymer yield were under 10%. All the reactivity ratios for the

Scheme 1 Synthesis of silicon-containing St-MI copolymer.

TMMS : R$_1$= R$_2$=—CH$_3$ **BMMS** : R$_1$=—CH$_3$, R$_2$=—C(CH$_3$)$_3$

TPMS : R$_1$= R$_2$=—⟨◯⟩   **TEMS** : R$_1$= R$_2$=—C$_2$H$_5$

TABLE II
Reactivity Ratios of Styrene (M$_1$) and Silicon-Containing MI (M$_2$) Monomers

Monomer (M$_2$)	Fineman–Ross		Kelen–Tüdos		Tidwell–Mortimer	
	r_1	r_2	r_1	r_2	r_1	r_2
TPMS	0.48	0.61	0.45	0.57	0.47	0.58
BMMS	0.56	0.59	0.54	0.57	0.55	0.58
TEMS	0.58	0.55	0.56	0.53	0.57	0.54
TMMS	0.61	0.52	0.59	0.48	0.60	0.49

above-mentioned copolymerization already produce the change from nearly 0 to 0.48–0.61, and is larger than that of the general St-MI copolymerization.[22–25] This was mainly due to the electron-withdrawing effect of silane side-chains to inhibit the carbonyl pairs withdrawing electron effect of double bond within MI. The result of the reducing reversed polarity of double bond of silicon-containing MIs relative to that of styrene indicated that the above-mentioned comonomers reaction is an azeotropic copolymerization, and is similar to the results of the composition ratios of copolymers versus those of feeds shown in Table I. As shown in Table II, the reactivity order of styrene-terminated radical toward the four series of silicon-containing monomers was TPMS > BMMS > TEMS > TMMS, indicating that these copolymerizations were also affected by the properties of different silicon-containing side chains within MI monomers. Since TPMS monomers had more phenyl rings around silicon atom, the interference caused by side chains on the electron-withdrawing effect of carbonyl pairs might be reduced. Therefore, the unsaturated double bonds of TPMS monomers should have a lower electron cloud density than that of the other MI monomers. All the molecular weight, molecular weight distribution, or comonomer's reactivity ratio should be, therefore, affected by both steric hindrance and polarity factors of silicon-containing side chains simultaneously.

Thermal properties of copolymers

Glass transition temperature

Glass transition temperature (T_g) of copolymers is one of the important physical properties that may be affected by their composition and morphology. All the T_g data of the four series of copolymers are given in Table III. Since the molecular weights of all the four series of copolymers were higher than 6.3×10^4 (see Table I), the effect of molecular weight on T_g was not significant. The DSC measurement for all the copolymers showed that all St-MI copolymers had a single T_g that would increase along with the increasing MI content. This means that MI segments and styrene segments within the copolymers exhibited a high

compatibility. Theoretically, T_g of the copolymers should comply with the Fox equation:[32]

$$\frac{1}{T_g} = \frac{W_1}{T_{g1}} + \frac{W_2}{T_{g2}} \tag{1}$$

where W_i was the weight fraction of comonomer i within the copolymer and T_{gi} was the homopolymer's T_g of comonomer i.

By substituting T_{gi} into eq. (1), the real T_g's of copolymers matching the Fox theory could be obtained. The relationships between the Fox's T_g curve and actual T_g

TABLE III
Glass Transition Temperatures of Copolymers Prepared from Styrene (M$_1$) and Silicon-Containing MI (M$_2$) Monomers

Copolymer	f_2[a]	W_2[b]	T_g (°C)[c]	T_g (K)	T_{g12} (K)[d]
St/TPMS	0.00	0.00	98	371	
	0.20	0.52	155	428	386
	0.31	0.66	159	432	
	0.46	0.79	161	434	
	0.49	0.81	162	435	
	0.58	0.86	163	436	
	0.72	0.92	165	438	
	0.86	0.96	172	445	
	1.00	1.00	183[e]	456	
St/BMMS	0.00	0.00	98	371	
	0.16	0.36	129	402	370
	0.30	0.56	140	413	
	0.45	0.70	143	416	
	0.48	0.73	145	418	
	0.58	0.81	147	420	
	0.71	0.88	152	425	
	0.85	0.94	158	431	
	1.00	1.00	169[e]	442	
St/TEMS	0.00	0.00	98	371	
	0.15	0.34	125	398	372
	0.30	0.56	136	409	
	0.44	0.70	140	413	
	0.47	0.72	141	414	
	0.57	0.79	145	418	
	0.70	0.87	149	422	
	0.84	0.94	155	428	
	1.00	1.00	165[e]	438	
St/TMMS	0.00	0.00	98	371	
	0.14	0.29	126	399	366
	0.29	0.51	139	412	
	0.43	0.65	142	415	
	0.46	0.68	144	417	
	0.56	0.76	147	420	
	0.69	0.85	153	426	
	0.82	0.92	161	434	
	1.00	1.00	172[e]	445	

[a] Mole fraction of M$_2$ within the copolymer.
[b] Weight fraction of M$_2$ within the copolymer.
[c] The glass transition temperature (T_g) is analyzed by DSC at a heating rate of 10°C/min under N$_2$.
[d] Glass transition temperature calculated by the modified equation of Johnston.
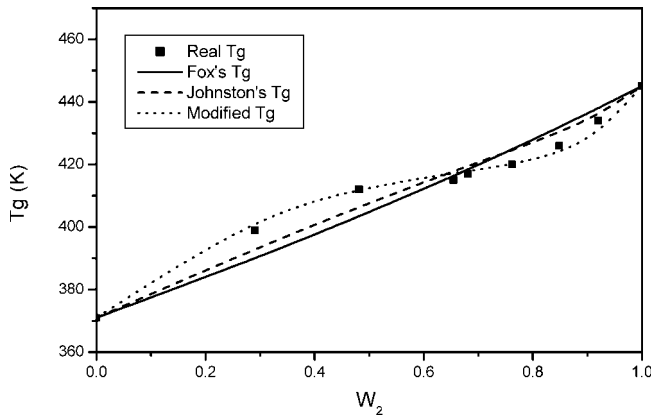[e] The data of homopolymers were used from the previous study (Ref. 26).

Figure 2 Variation of T_g as a function of the weight fraction of TMMS (W_2) for the St-MI copolymer system.

values, measured by DSC, versus the copolymer compositions are shown in Figures 2–5. Considering the segment structure of MIs, although their silicon-containing side chain was a highly mobile segment, molecular motions of these segments could only proceed under a relatively higher temperature or energy because of the high rigidity of the imide structure. As shown in Table III, the T_g's of MI homopolymer and all the copolymers were higher than that of polystyrene, indicating that the rigid degree of the former was higher than that of the latter. In Figures 2–5, the actual T_g curves of copolymers, in comparison with the Fox's curves, exhibited the positive/negative deviations. The S-like curve of T_g in blending polymer system had also been studied in literature.[33] The T_g of the alternating segments within copolymer (T_{g12}) should affect the T_g of the overall copolymer significantly. Besides, each of the four series of copolymers had a T_g value conformed to match the Fox theory (the value at the intersection with Fox's curve), postulating that the comonomer segment distribution for copolymer in azeotropic composition was more random than that in the others, leading to the offset of the alternate segment effect.
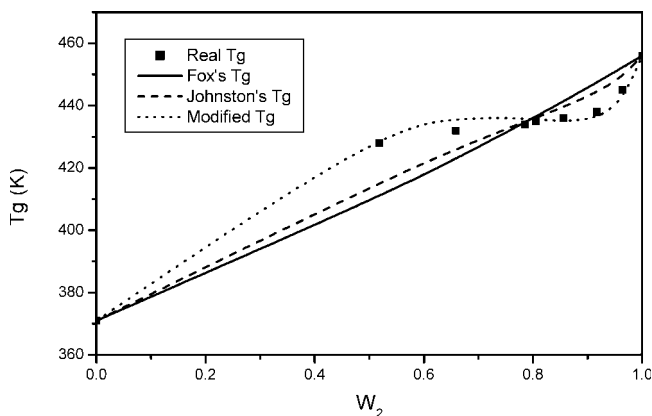

Figure 3 Variation of T_g as a function of the weight fraction of TPMS (W_2) for the St/MI copolymer system.
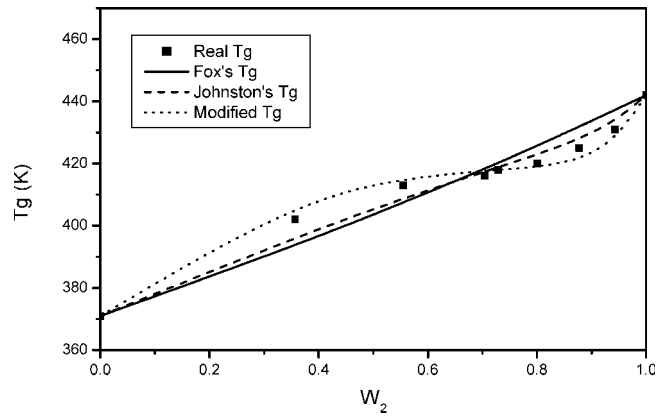

Figure 4 Variation of T_g as a function of the weight fraction of BMMS (W_2) for the St/MI copolymer system.

On the other hand, except the copolymer with azeotropic composition, the molecular motion of the others was easily affected by its alternate segment. Therefore, a higher content of silicon-containing MI segment within copolymer would produce a negative deviation of T_g due to the effect of styrene segment, and on the contrary, a lower content would produce a positive deviation of T_g due to the effect of MI segment. To understand the effect of the alternate segment for the actual T_g's of copolymers, the Johnston's equation[34] modified from Fox theory was applied:

$$\frac{1}{T_g} = \frac{W_1 P_{11}}{T_{g11}} + \frac{W_2 P_{22}}{T_{g22}} + \frac{W_1 P_{12} + W_2 P_{21}}{T_{g12}} \qquad (2)$$

where P_{ij} is the probability of forming ij-segment, T_{gii} the homopolymer's T_g of comonomer i, and T_{gij} the glass transition temperature of alternating segment within copolymer. The P_{ij} could be calculated as

$$P_{12} = \frac{1}{1 + r_1 \frac{[1]}{[2]}} = \frac{1}{1 + r_1 \frac{f_1}{f_2}} \qquad P_{21} = \frac{1}{1 + r_2 \frac{[2]}{[1]}} = \frac{1}{1 + r_2 \frac{f_2}{f_1}}$$
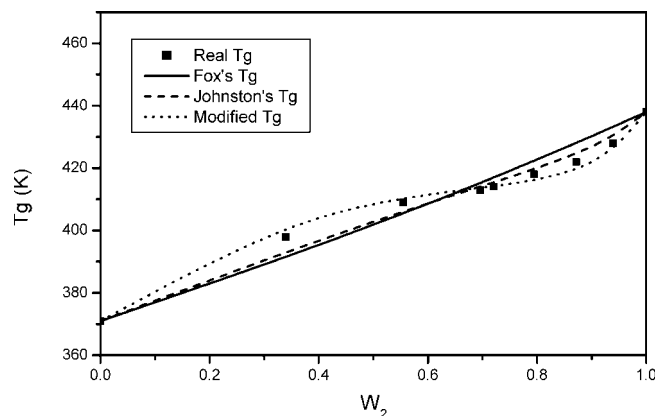
$$P_{11} = 1 - P_{12} \qquad P_{22} = 1 - P_{21}$$

Figure 5 Variation of T_g as a function of the weight fraction of TEMS (W_2) for the St/MI copolymer system.

TABLE IV
Thermal Properties of Copolymers Prepared from Styrene (M_1) and Silicon-Containing MI (M_2) Monomers

Monomer (M_2)	F_2[a]	f_2[b]	Si (%)[c]	5 wt % Loss ($T_{5\%}$,°C)[d]		Char at 800°C (%)[d]	
				N_2	Air	N_2	Air
TPMS	0.00	0.00	0.0	373	323	0.0	0.0
	0.10	0.20	3.2	375	328	8.9	0.4
	0.25	0.31	4.1	377	335	12.3	1.3
	0.50	0.49	5.0	379	345	15.1	1.6
	0.75	0.72	5.7	381	356	18.2	2.0
	0.90	0.86	6.0	383	373	21.5	2.5
	1.00	1.00	6.3	385	380	22.9	2.8
BMMS	0.00	0.00	0.0	373	323	0.0	0.0
	0.10	0.16	3.3	373	324	9.1	1.8
	0.25	0.30	5.1	372	326	15.5	3.1
	0.50	0.48	6.7	371	332	18.7	3.5
	0.75	0.71	8.1	370	341	20.6	5.1
	0.90	0.85	8.7	368	347	22.3	5.7
	1.00	1.00	9.6	367	351	25.5	6.9
TEMS	0.00	0.00	0.0	373	323	0.0	0.0
	0.10	0.15	3.14	373	328	11.1	1.5
	0.25	0.30	3.53	374	333	12.6	2.1
	0.50	0.47	6.66	375	342	18.5	3.9
	0.75	0.70	8.06	376	351	20.3	4.6
	0.90	0.84	8.67	377	365	22.5	5.0
	1.00	1.00	9.30	377	372	26.6	5.4
TMMS	0.00	0.00	0.0	373	323	0.0	0.0
	0.10	0.14	3.1	374	327	8.4	0.5
	0.25	0.29	5.4	375	332	17.2	2.9
	0.50	0.46	7.3	376	338	21.1	4.2
	0.75	0.69	9.1	378	342	25.8	6.2
	0.90	0.82	9.9	380	348	29.3	7.7
	1.00	1.00	10.7	384	352	31.3	12.0

[a] Mole fraction of M_2 in the feed.
[b] Mole fraction of M_2 within the copolymer.
[c] The theoretical calculation values of Si composition ratio.
[d] Thermal properties are analyzed by TGA at a heating rate of 20°C/min under N_2 or air.

It could also be seen in Figures 2–5 that the Johnston's curves of copolymers did not match the actual T_g curves. That means the effect of its T_{g12} on the real T_g of copolymer cannot be sufficiently described by Johnston's equation. Considering the influence of T_{g12} that should be more significant, a modified Johnston's equation can be taken as follows:[35]

$$\frac{1}{T_g} = \frac{W_1 P_{11}}{T_{g11}} + \frac{W_2 P_{22}}{T_{g22}} + \frac{W_1^\alpha P_{12} + W_2^\alpha P_{21}}{T_{g12}} \quad (3)$$

where α is a parameter according to the effect of alternating segment. Substitution of actual T_g of all the four series of copolymers into eq. (3) gave an average of T_{g12} so as to obtain the modified $T_g - W_2$ curves. The value α was determined by a trial-and-error method so as to make the modified $T_g - W_2$ curves approach the actual T_g as possible as it can be. It could also be seen from Figures 2–5 that the actual T_g of all

the four series of copolymers were proved to match our modified curves while $\alpha = 1.24$ in TMMS, $\alpha = 1.28$ in TPMS, $\alpha = 1.23$ in BMMS, and $\alpha = 1.20$ in TEMS series. That means the T_g of these copolymers could be sufficiently described by our modified equation as a result of increasing the effect of weight ratio on T_{g12}.

Thermal stability

Thermal properties of four series St-MI copolymers measured by TGA under N_2 or air are listed in Table IV. Thermal stability of four kinds of MI-homopolymers had been discussed in the previous study.[26] $T_{5\%}$ of all the MI homopolymers with different silicon-containing groups was higher than 367°C when heated under nitrogen gas. The groups of TPMS with a higher phenyl density exhibited a higher thermal decomposition temperature, around 385°C. The groups of BMMS with a larger alkyl side-chain, on the contrary, exhibited a lower thermal decomposition temperature.

The TGA traces of St-TPMS copolymers measured under nitrogen and air are shown in Figure 6 and 7, respectively. The scission of all the copolymers under nitrogen and air was a one-stage and a two-stage process, respectively. Decomposition reactions under N_2, as shown in Figure 6, should be initialized mainly by scission of silane side-chains, and further produced scission of the MI and styrene main-chain along with carbonization to form char yield of solid residue. Thermal stability of all the St-MI copolymers under N_2 was higher than under air because of the oxidization reaction. When all copolymers were heated in air, decomposition, as shown in Figure 7, changed from one-stage to two-stage. The decomposition of the second stage should be the oxidized combustion reaction under the high temperature. Although the char yield of the St-TPMS copolymer pyrolyzed under air was not obviously increased with increasing the silicon content, the maximum rates of weight loss of these polymers were
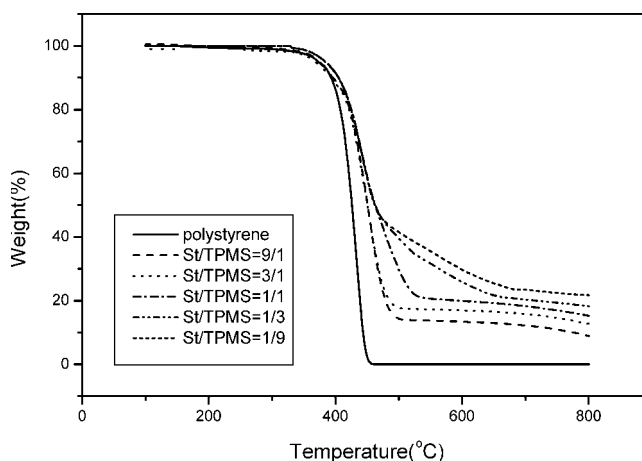

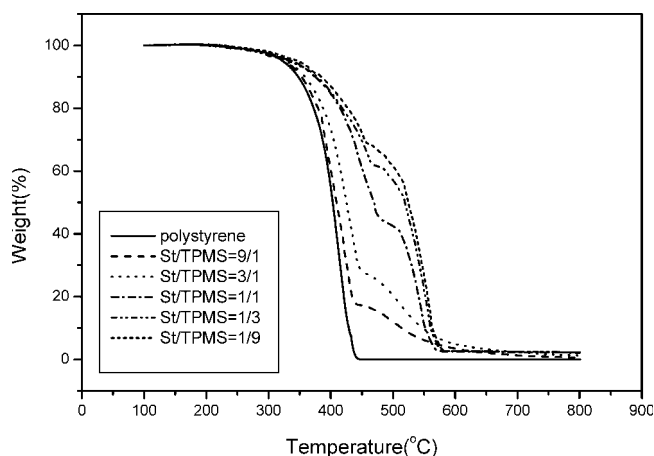**Figure 6** TGA traces of Styrene-TPMS copolymers under N_2.

Figure 7 TGA traces of styrene-TPMS copolymers in air.

decreased and the pyrolysis curves moved to higher temperature as the silicon content was increased. The results of lower weight loss rates during pyrolysis of silicon-containing system still showed that the introduction of silane side-chain into copolymers improved flame retardancy.

The TGA traces of four MI-series copolymers measured under nitrogen and air are alike. When compared to the $T_{5\%}$ in Table IV, the thermal stability of each copolymer series was higher than that of styrene homopolymer. The initial temperature of pyrolysis of all the four series copolymer was generally increased with increasing the MI content. This means that the silicon-containing side chains could increase thermal stability of copolymers under nitrogen or air. Also, the char yield of all the four series copolymers was generally increased with increasing the silicon content both under N_2 and air. The higher char yield and lower weight loss rates showed that the introduction of silane side-chain into polymers improved flame retardancy.

CONCLUSIONS

The radical copolymerizations of styrene with four silicon-containing MIs were carried out to get the azeotropic copolymers. The factors, such as steric hindrance and chain transfer caused by silicon-containing MI, could affect the molecular weight, distribution index, and segments distribution of copolymer. The actual T_g's curves versus the composition ratios for all the above-mentioned copolymers were very consistent with the modified Johnston's equation as increasing the weight ratio of alternate segments. The maleimide segments and styrene segments within these copolymers exhibited good compatibility and the thermal stability and flame retardancy of polystyrene could be enhanced simultaneously via the introduction of silicon-containing maleimide.

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