e-Polymers **2007**, no. 128

http://www.e-polymers.org
ISSN 1618-7229

Studies of silicon-containing maleimide polymers. Part II: Synthesis and properties of poly(styrene-*co*-bromine-containing maleimide).

*Chia-Yu Chiang, Ruey-Shi Tsai, and Wei-Jye Shu**

*Department of Chemical and Material Engineering, Ta-Hwa Institute of Technology, 1, Ta-Hwa Road, Chiung-Lin, Hsinchu 30743, Taiwan, ROC; fax : 886-3-5927310; e-mail : shu@thit.edu.tw)

(Received: 22 June, 2007; published: 7 November, 2007)

Abstract: Soluble copolymers of a series of bromine-containing (N-maleimido phenoxy) silane (BMS) monomers with styrene (St) were synthesized by radical polymerization in toluene using 2,2'-azobisisobutyronitrile (AIBN) 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 calorimetry (DSC) and thermo-gravimetric analysis (TGA) respectively. The introduction of silane side-chain into maleimide (MI) monomers changed the comonomer reactivity ratio with styrene from alternating to azeotropic copolymerization. The curves of T_g's versus the different compositions of the above synthesized St-BMS copolymers matched a modified T_g's equation as a increase in the effect of weight ratio on alternating-segment, and 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 flame retardancy of polystyrene could be enhanced via the introduction of Si/Br-containing maleimide.

Keywords: poly(styrene-*co*-maleimide) ; copolymerization ; reactivity ratio ; flame retardancy

Introduction

Polystyrene is a general commodity polymer widely used in a range of applications. For many of these, the presence of an additive or any structure-modification to impart some flammability resistance is required. Most commonly, brominated aromatics are used for this purpose. Brominated flame retardants are used for fire precautions with the purpose of protecting human life, health and property. As the polymer undergoes combustion, these compounds decompose to generate bromine atoms and/or hydrogen bromide which escapes to the gas phase to trap flame propagating radicals and interrupt the combustion reaction schemes to get a higher flame resistance effect. Traditional flame retarding polymers are prepared from the physical blending with brominated additives [1, 2]. Because of the restrictions in applications for some reasons such as processing or physical properties, the studies of flame retardants have gradually changed from additive type to reactive type such as structural modification by copolymerizing with brominated aromatic monomer [3, 4], crosslinking with brominated resin [5], membranes coated with brominated polymers [6], surface bromination [7], and bromine doping [8]. Although they present the opportunity for loss of halogen, smoke and toxic substance to the atmosphere and so as to be limited in some parts of the world (such as WEEE & RoHS), brominated flame retardants are still the most effective in inhibiting flame propagation.

Maleimide 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 maleimide monomers also provide some desirable properties. Up to now, applications of N-substituted maleimide polymers include photo-resistance with high T_g [9, 10], flexibilizer for thermosetting polymers [11-14], non-linear polymer with high T_g and flame retardancy etc [15]. Some N-protected polymaleimides have been investigated for their applicability as thermally-stable resist materials in the deep ultraviolet (DUV) region based on the chemical amplification concept [16-19].

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. A lot of work about the AM copolymers, such as the copolymers with styrene [20-22], has been reported so far. These copolymers were synthesized by introducing the rigid and high thermal stability of AM segment leading to 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 nearby 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 [23-26]. But, the silicon-containing AM systems are still rarely seen in literature [27, 28].

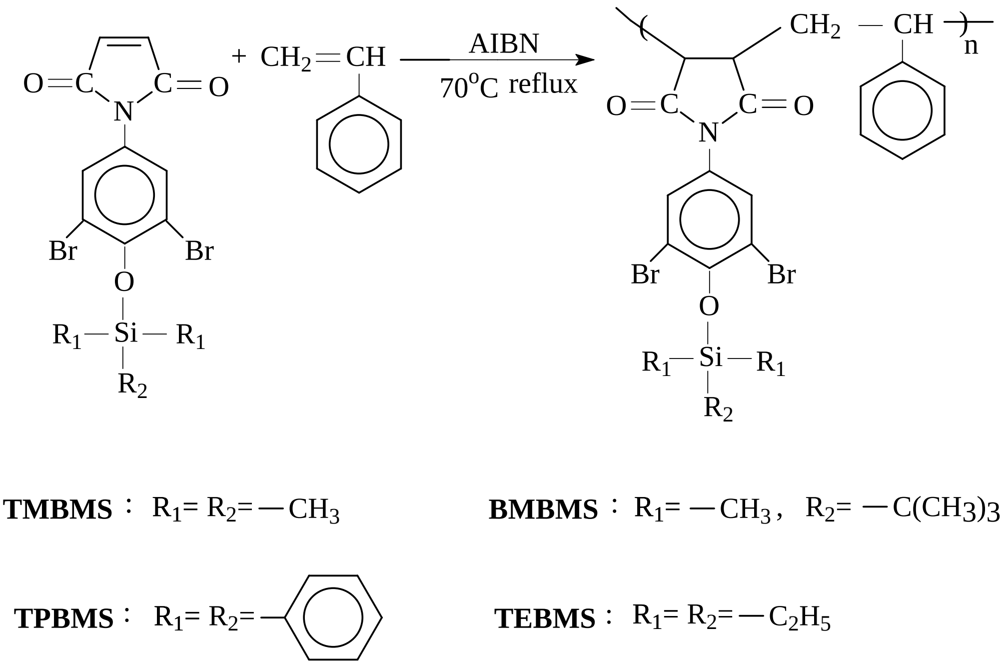
Our team has already designed a series of different silicon-containing side chains which was introduced into N-aryl maleimides with high thermal stability, which could be polymerized by free radical initiator to form soluble homopolymer [29]. In this paper we will discuss the reactivity ratios of styrene and four Si/Br-containing N-aryl maleimide pairs in copolymerization to study their copolymerized behaviors. The thermal stabilities and flame retardancy of the above synthesized copolymers are also discussed.

Results and Discussion

Copolymerization and Copolymer Properties

The copolymers of styrene with BMS monomers were synthesized by radical polymerization in toluene solution using AIBN as initiator as shown in Scheme 1.

The FTIR spectra of St-TMBMS(50%), St-TPBMS(50%), and St-BMBMS(50%) copolymers, as shown in Fig 1, revealed the absorption bands ν(cm^{-1}): 1706 cm^{-1} (C=O), 1597, 1520 cm^{-1} (C=C from benzene), 831 (di-substitution of benzene), 1414 cm^{-1} (C-N-C), 1240 cm^{-1} (Si-CH_3), and 1080 cm^{-1} (-Si-O) from N-phenylmaleimide; 1430 (Si-C_6H_5, from TPBMS); 1350(-$C(CH_3)_3$, from BMBMS) and 700(mono-substitution of benzene) from styrene. Besides, the chemical shift (δ) of –CH– within styrene unit in St/TMBMS copolymer measured from ^{13}C-NMR and ^{1}H-NMR (d-chlorofom) appear at about 42.2 ppm and 3.9 ppm, the 2-**C**=O/4'-**C**-O-Si/ -CO-**C**H-**C**H-CO-/3',5'-**C/**1'-**C**-N-/2',6'-**C/**Si-**C**H_3 within TMBMS unit measured from ^{13}C-NMR($CDCl_3$) appear at 171.5/152.0/135.8/133.1/111.7/116.3/22.5 ppm also conforming that these copolymers were synthesized successfully.



Scheme 1. Synthesis of St-BMS copolymer.

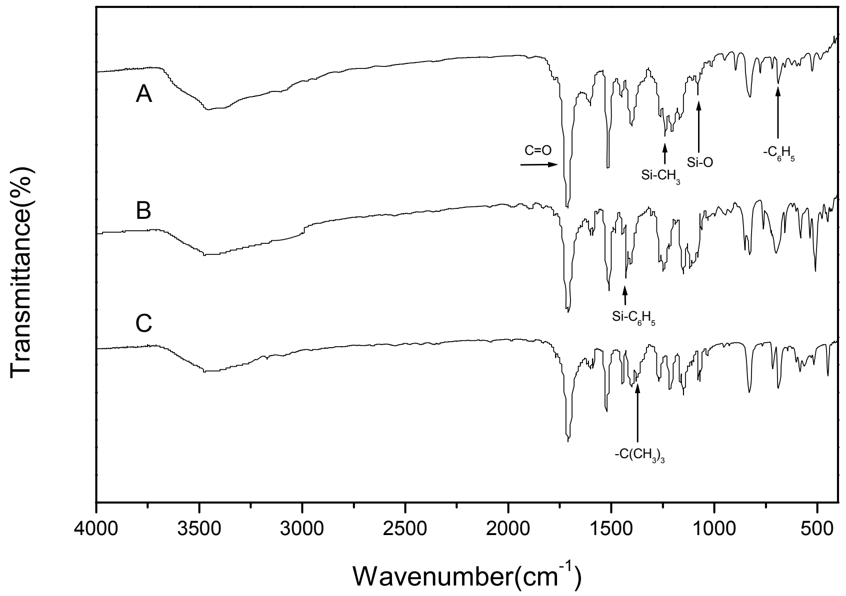


Fig. 1. The FTIR spectra of A : St-TMBMS(50%), B : St-TPBMS(50%), and C : St-BMBMS(50%) copolymers.

Basic properties of St-BMS copolymers in different BMS contents and molecular weights obtained from elemental analysis and GPC analysis are given in Table 1. The average number molecular weights ($\overline{Mn}$) of each copolymer series were approximately in the range 7.9~11.9×10^4 (g/mol). The $\overline{Mn}$ gradually decreased, while the distribution index of molecular weight increased along with the increase in BMS monomers in feed. This might be due to the low homopolymerizability of maleimide.

Besides, the copolymerization degree and average molecular weight might be affected by the side-chain effect and steric hindrance generated from Br/Si-containing maleimide segments. The sequence of intermolecular steric hindrance should be TPBMS>BMBMS>TEBMS>TMBMS. Also, since St-TPBMS series copolymers would form a larger steric hindrance during copolymerization due to TPBMS monomers, a lower polymerization degree and a lower average molecular weight would be obtained.

Tab. 1. Properties of copolymers prepared from styrene(M_1) and BMS monomers(M_2).

Monomer (M_2)	F_2 [a]	Conversion (%)	f_2 [a]	$\overline{Mw}$ [b] ($\times 10^4$)	$\overline{Mn}$ [b] ($\times 10^4$)	$\overline{Mw}/\overline{Mn}$
TPBMS	0.90	9.2	0.85	29.5	7.9	3.73
	0.75	9.1	0.71	31.2	8.5	3.67
	0.60	9.1	0.58	32.3	9.0	3.59
	0.50	8.9	0.49	32.8	9.3	3.53
	0.40	8.2	0.45	33.6	9.6	3.50
	0.25	8.8	0.30	34.9	10.3	3.39
	0.10	8.1	0.19	35.2	10.6	3.32
BMBMS	0.90	8.2	0.86	31.9	8.6	3.71
	0.75	8.3	0.71	33.2	9.1	3.65
	0.60	8.5	0.57	34.1	9.6	3.55
	0.50	8.9	0.48	34.5	9.9	3.48
	0.40	7.5	0.44	35.3	10.3	3.43
	0.25	7.6	0.29	36.1	10.8	3.34
	0.10	8.3	0.15	36.5	11.1	3.29
TEBMS	0.90	8.2	0.85	32.5	8.9	3.65
	0.75	8.1	0.70	34.0	9.4	3.62
	0.60	8.2	0.56	35.4	10.0	3.54
	0.50	8.8	0.47	36.1	10.4	3.47
	0.40	7.9	0.44	36.2	10.6	3.42
	0.25	7.8	0.29	37.1	11.1	3.34
	0.10	8.5	0.14	37.4	11.5	3.25
TMBMS	0.90	8.1	0.83	32.8	9.1	3.60
	0.75	8.3	0.70	34.2	9.5	3.61
	0.60	8.2	0.56	35.8	10.1	3.54
	0.50	8.0	0.46	36.4	10.5	3.47
	0.40	7.8	0.43	36.8	10.8	3.41
	0.25	7.8	0.28	38.1	11.4	3.34
	0.10	8.2	0.13	38.3	11.9	3.22

[a] F_2 and f_2 are the mole fraction of M_2 in the feed and in the copolymers while f_2 are obtained from element analysis.

[b] Distribution of molecular weights are tested by GPC with a concentration of 0.5wt% in THF.

The double bond of N-phenyl maleimide as a result of the electron-withdrawing effect between carbonyl groups on both sides would generally show its reversed polarity versus styrene monomers [31]. This means the unsaturated double bonds of N-phenyl maleimide will be in a state of poor-electron and that of styrene in a relatively rich-electron state. Then, there is a high tendency for them to be copolymerized to generate alternating-like St-MI copolymers with the reactivity ratios approaching to zero. The reactivity ratios of styrene-BMS comonomers, as shown in Table 2, were determined by the method of Fineman-Ross [32], Kelen-Tüdos [33], and Tidwell-Mortimer [34] while all the instantaneous copolymer yield were under 10%. All the reactivity ratios for the above copolymerization already produced the change from nearby zero to 0.47-0.68, and were larger than that of the general St-MI copolymerization. This was mainly due to the electron-withdrawing effect of Br/Si-containing side-chains to inhibit the carbonyl pairs withdrawing electron effect of double bond within maleimide. The result of the reducing reversed polarity of double bond of Br/Si-containing maleimides relative to that of styrene indicated that the above 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 1. As shown in Table 2, the reactivity orders of styrene-terminated radical towards the 4 series of Br/Si-containing monomers was TPBMS>BMBMS>TEBMS >TMBMS, indicating that these copolymerizations were also affected by the properties of different Br/Si-containing side chains within BMS monomers.

Tab. 2. Reactivity ratios of styrene (M_1) and BMS monomers(M_2).

Monomer (M_2)	Fineman-Ross		Kelen-Tüdos		Tidwell-Mortimer	
	r_1	r_2	r_1	r_2	r_1	r_2
TPBMS	0.54	0.53	0.50	0.47	0.52	0.49
BMBMS	0.59	0.59	0.54	0.56	0.57	0.57
TEBMS	0.64	0.60	0.58	0.56	0.61	0.56
TMBMS	0.68	0.61	0.65	0.53	0.67	0.55

Since TPBMS 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 TPBMS monomers should have a lower electron cloud density than that of the other BMS 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 Br/Si-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 4 series of copolymers are given in Table 3. Since the molecular weights of all the 4 series of copolymers were higher than 7.9×10^4 (see Table 1), the effect of molecular weight on T_g was not significant. The DSC measurement for all the copolymers showed that all St-BMS copolymers had a single T_g that would increase along with the increasing maleimide content. This means that maleimide-segments and styrene-segments within the copolymers exhibited a high compatibility.

Tab. 3. Glass transition temperatures of copolymers prepared from styrene (M_1) and BMS monomers(M_2).

Copolymer			$T_g(^oC)$[c]		$T_{g12}(K)$[d]
	f_2[a]	W_2[b]		$T_g(K)$	
St-TPBMS	0.00	0.00	98	371	379
	0.19	0.58	139	412	
	0.30	0.71	149	422	
	0.45	0.83	151	424	
	0.49	0.85	155	428	
	0.58	0.89	157	430	
	0.71	0.93	164	437	
	0.85	0.97	167	440	
	1.00	1.00	179	452	
St-BMBMS	0.00	0.00	98	371	365
	0.15	0.44	131	404	
	0.29	0.64	137	410	
	0.44	0.78	139	412	
	0.48	0.80	140	413	
	0.57	0.85	142	415	
	0.71	0.92	146	419	
	0.86	0.96	151	424	
	1.00	1.00	164	437	
St-TEBMS	0.00	0.00	98	371	369
	0.14	0.42	132	405	
	0.29	0.64	137	410	
	0.44	0.78	139	412	
	0.47	0.80	140	413	
	0.56	0.85	142	415	
	0.70	0.91	147	420	
	0.85	0.96	150	423	
	1.00	1.00	160	433	
St-TMBMS	0.00	0.00	98	371	366
	0.13	0.38	128	401	
	0.28	0.61	139	412	
	0.43	0.75	142	415	
	0.46	0.77	143	416	
	0.56	0.84	145	418	
	0.70	0.90	149	422	
	0.83	0.95	157	430	
	1.00	1.00	167	440[e]	

[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 in N_2

[d] Glass transition temperature calculated by the modified T_g-equation.

[e] The data of homopolymers were used from the previous study(ref.29).

Theoretically, T_g of the copolymers should comply with the Fox equation[35] :

$$\frac{1}{Tg}=\frac{W_1}{Tg_1}+\frac{W_2}{Tg_2} \qquad (1)$$

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 equation (1), the real T_gs of copolymers matching the Fox theory could be obtained.

The relationships between the Fox's T_g-curve and actual T_g's values, measured by DSC, versus the copolymer compositions are shown in Fig 2-5. Considering the segment structure of TMBMS, although its silicon-containing side chain was high mobile segment, molecular motions of these segments could only proceed under a relatively higher temperature or energy due to the high rigidity of the imide structure.

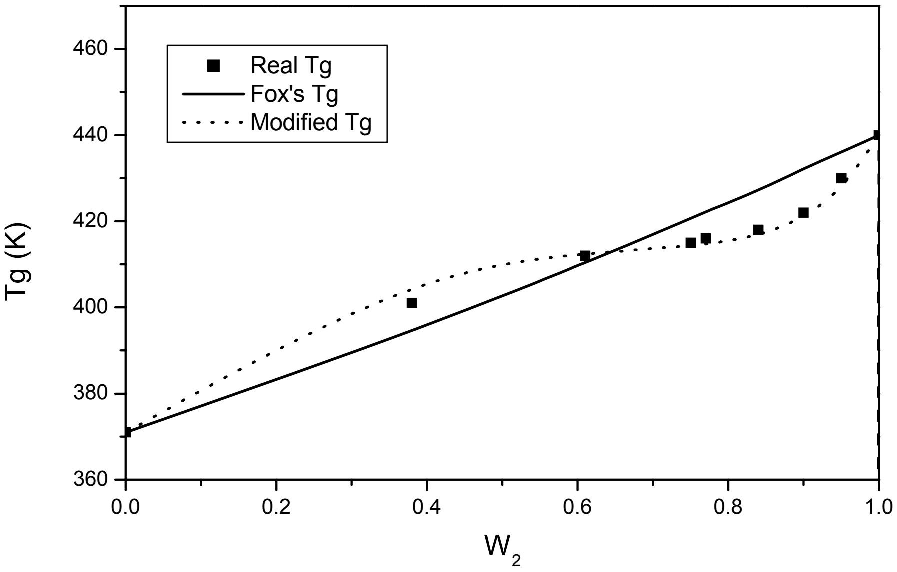


Fig. 2. Variation of T_g as a function of the weight fraction of TMBMS (W_2) for the St-BMS copolymer system.

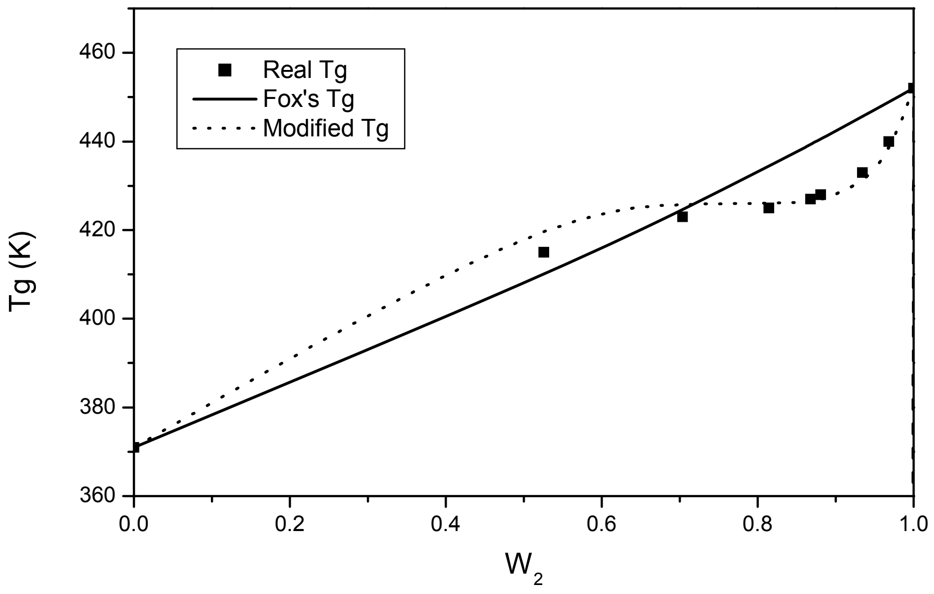


Fig. 3. Variation of T_g as a function of the weight fraction of TPBMS (W_2) for the St-BMS copolymer system.

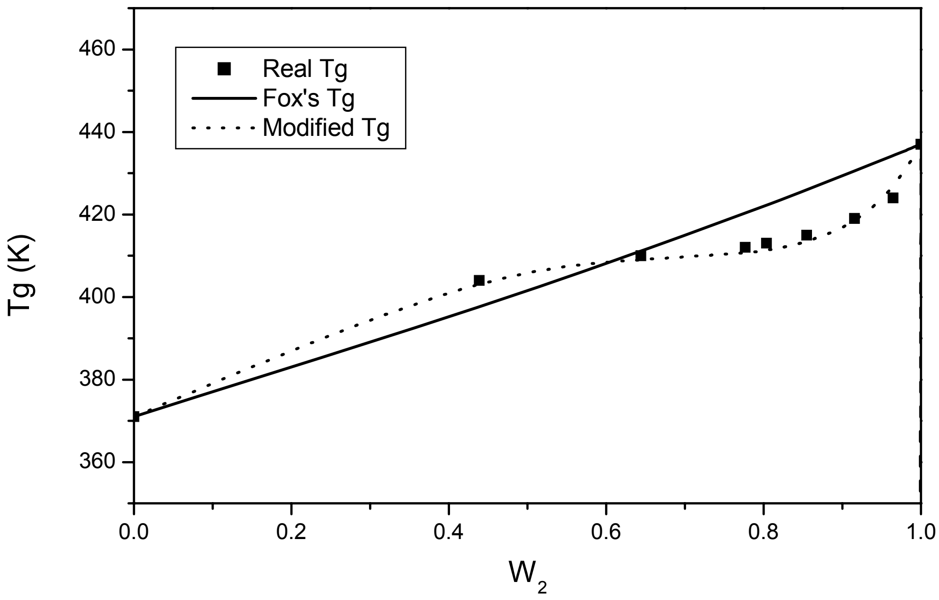


Fig. 4. Variation of T_g as a function of the weight fraction of BMBMS (W_2) for the St-BMS copolymer system.

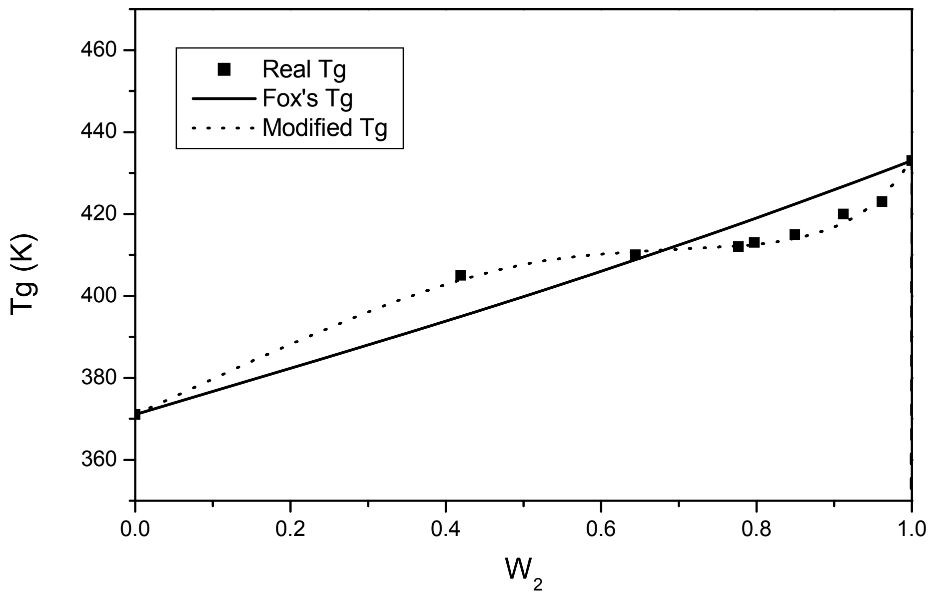


Fig. 5. Variation of T_g as a function of the weight fraction of TEBMS (W_2) for the St-BMS copolymer system.

As shown in Table 3, the T_g's of TMBMS homopolymer and all the copolymers were higher than that of polystyrene series, indicating that the rigid degree of the former was higher than that of the latter. In Fig. 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 [36]. 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 4 series 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 offset the alternate segment effect. 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 Br/Si-containing maleimide 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 maleimide segment.

In order to understand the effect of the alternate segment for the actual T_gs of copolymers, a T_g-equation modified from Fox theory and Johnston's equation [37] was applied [38]:

$$\frac{1}{Tg} = \frac{W_1 P_{11}}{Tg_{11}} + \frac{W_2 P_{22}}{Tg_{22}} + \frac{W_1^{\alpha} P_{12} + W_2^{\alpha} P_{21}}{Tg_{12}} \tag{2}$$

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

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

could be calculated as:

where α is a parameter according to the effect of alternating segment. Substitution of actual T_g of all the 4 series copolymers into the equation (2) 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 approaching to the actual T_g as possible as it can be. It could also be noticed from Fig 2-5 that the actual T_g of all the 4 series of copolymers were proved to match our modified curves while α=1.26 in TMBMS, α=1.29 in TPBMS, α=1.24 in BMBMS, and α=1.24 in TEBMS 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}.

$$P_{11} = 1 - P_{12} \qquad\qquad P_{22} = 1 - P_{21}$$

-Thermal Stability

Thermal properties of 4 series St-BMS copolymers measured by TGA in N_2 or air are listed in Table 4. The TGA traces of St-TPBMS copolymers measured in nitrogen and air are shown in Fig 6 and Fig 7, respectively. The scission of all the copolymers in nitrogen and air was a 2-stage and a 3-stage process, respectively. Since the bromine atoms within the BMS comonomer exhibit a poor thermal stability and occupy a large weight percentage in itself, the decomposition of copolymers should be initialized by the scission of bromine-containing bonding position in the first stage. And then, as shown in Fig 6, the following decomposition mechanisms in the second stage are scission of the maleimide and styrene main-chain along with carbonization to form char yield of solid residue. The char yield of St-TPBMS copolymer increased with increasing the Si/Br content in N_2. Thermal stability of all the St-BMS copolymers in N_2 was higher than that in air because of the oxidization reaction. When all copolymers were heated in air, decomposition, as shown in Fig 7, changed from 2-stage to 3-stage.

Tab. 4. Thermal properties of copolymers prepared from styrene (M_1) and BMS monomers (M_2)

Monomer (M_2)	F_2[a]	f_2[b]	Si(%)[c]	Br(%)[c]	5wt%Loss ($T_{5\%}$, °C)[d]		Char at 800°C (%)[d]	
					N_2	Air	N_2	Air
TPBMS	0.05	0.08	1.8	7.8	257	235	0.3	0.6
	0.10	0.19	3.0	13.4	256	234	3.3	1.0
	0.15	0.21	3.2	14.1	254	233	5.4	1.4
	0.20	0.24	3.4	15.1	252	230	12.7	2.0
	0.25	0.30	3.8	16.6	250	227	18.3	3.3
BMBMS	0.05	0.07	1.7	8.7	256	234	0.6	0.5
	0.10	0.15	3.0	15.2	254	229	13.2	2.2
	0.15	0.19	3.5	17.6	251	226	19.5	4.5
	0.20	0.22	3.8	19.2	249	224	21.2	5.8
	0.25	0.29	4.5	22.2	245	223	23.7	6.5
TEBMS	0.05	0.07	1.7	8.7	257	233	0.8	0.6
	0.10	0.14	2.9	14.5	255	232	6.1	1.6
	0.15	0.20	3.6	18.2	250	225	20.2	5.1
	0.20	0.23	3.9	19.7	248	223	21.8	5.9

	0.25	0.29	4.5	22.2	246	222	23.5	6.8
TMBMS	0.05	0.06	1.6	7.8	258	236	0.5	0.5
	0.10	0.13	2.9	14.3	254	232	5.9	1.8
	0.15	0.18	3.6	17.8	251	226	21.0	4.7
	0.20	0.22	4.1	20.2	249	222	22.1	6.1
	0.25	0.28	4.7	23.2	244	221	25.2	7.0

[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/Br composition ratio.

[d] Thermal properties is analyzed by TGA at a heating rate of 20°C/min in N_2 or air

The decomposition of the 3rd stage should be the oxidized combustion reaction under the high temperature. Although the char yield of the St-TPBMS copolymer pyrolyzed in air was not obviously increased with increasing the Si/Br content, the maximum rates of weight loss of these polymers were decreased and the pyrolysis curves moved to higher temperature as the Si/Br content was increased. The results of lower weight loss rates during pyrolysis of Si/Br-containing system still showed that the introduction of BMS-chain into copolymers improved flame retardancy.

The TGA traces of 4 BMS-series copolymers measured in nitrogen and air were alike. The scission of St-BMS copolymers in N_2 was a two-stage decomposition process. $T_{5\%}$ of all the BMS-copolymers with different Br/Si-containing groups was around 244-258 °C mainly due to the pyrolysis of bromine atoms. As compared in Table 4, the char yield of all the 4 series copolymer generally increased with increasing the Si/Br content both in N_2 and in air environment. The higher char yield and lower weight loss rates showed that the introduction of Br/Si-containing side-chain into polymers improved flame retardancy.

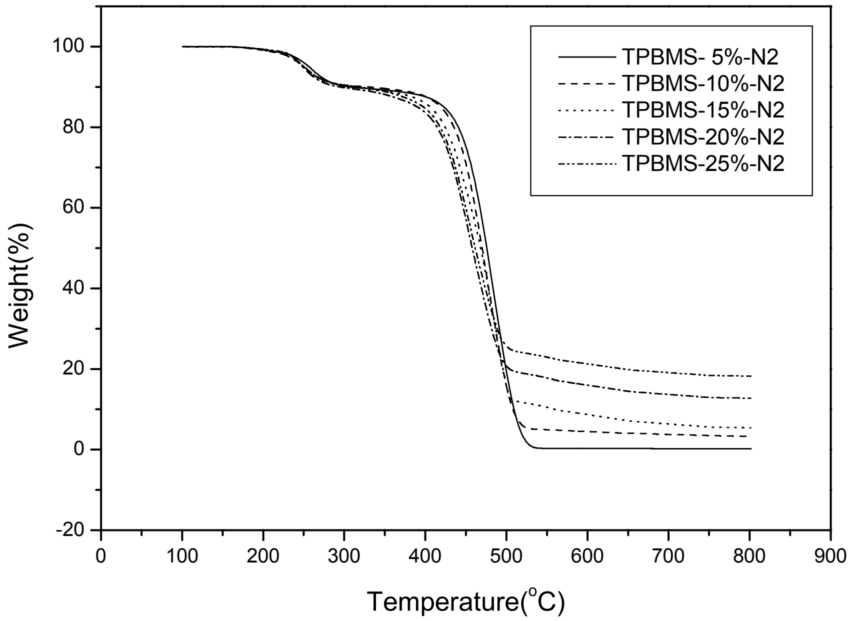


Fig. 6. TGA traces of Styrene-TPBMS copolymers in N_2.

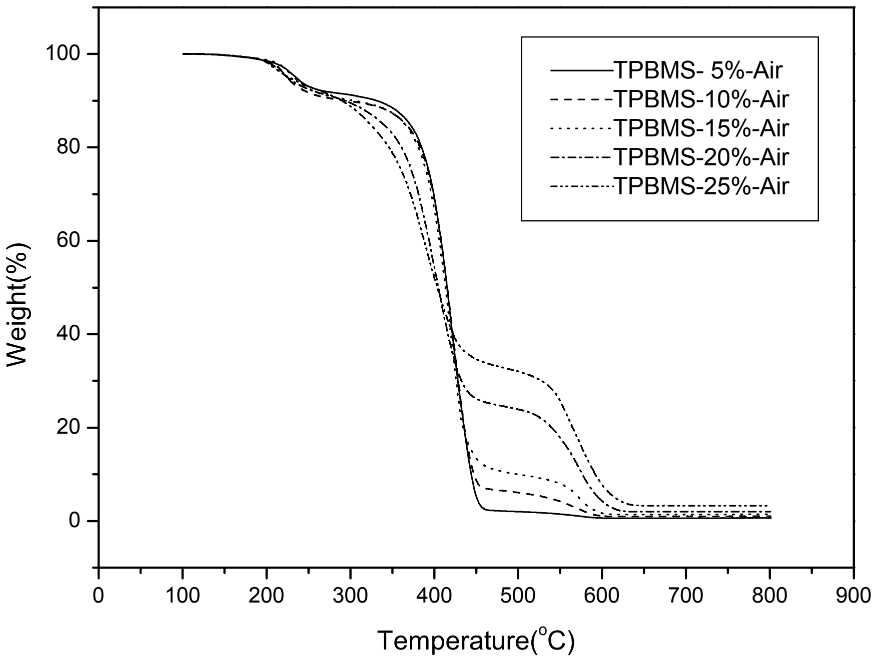


Fig. 7. TGA traces of Styrene-TPBMS copolymers in air.

Conclusions

The radical copolymerizations of styrene with 4 Br-containing maleimides were carried out to get the azeotropic copolymers. The factors, such as steric hindrance and low homopolymerizability caused by Si/Br-containing maleimide, could affect the molecular weight, distribution index and segment distribution of copolymer. The actual T_g's curves versus the composition ratios for all the above copolymers were very consistent with the modified T_g's equation as an increase in the weight ratio of alternate segments. The BMS-segments and styrene-segments within these copolymers exhibited good compatibility and the flame retardancy of polystyrene could be enhanced simultaneously via the introduction of Si/Br-containing maleimide.

Experimental part

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(2,6-dibromo-4-(N-maleimido) phenoxy) silane (TMBMS), triphenyl (2,6-dibromo-4-(N-maleimido) phenoxy) silane (TPBMS), t-Butyl dimethyl (2,6- dibromo-4-(N-maleimido) phenoxy) silane (BMBMS), and triethyl (2,6-dibromo- 4-(N-maleimido) phenoxy) silane (TEBMS) were prepared by the method described in our previous paper [29]. 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. These BMS monomers obtained were dried in vacuum. The characterization of the monomer synthesized was analyzed by the ^1H, ^{13}C, ^{29}Si

Nuclear Magnetic Resonance (NMR) spectroscopy, Fourier Transform Infrared Reflection (FTIR) spectroscopy and elemental analysis, respectively.

The initiator, 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 (DMF) was dried by CaH_2 over night. The other solvents were purified by conventional methods.

Synthesis of Copolymer

A flask was charged with various ratios of styrene and BMS monomers obtained as shown in Table 1, AIBN as initiator (5mmole/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% in order to satisfy the differential copolymerization equation [30]. The solvent was removed under reduced pressure, and then the polymerization mixture was again dissolved in dichloromethane and poured into a large amount of methanol. The copolymer then was isolated by filtration and dried under vacuum at 60 °C.

Instruments

The IR-spectra, ^{13}C and ^{1}H NMR spectra, and elemental analyses (C, H, N) of the St-BMS copolymers were obtained by a Nicolet Omnic 3 Fourier Transform Infrared Reflection (FTIR) spectroscopy, Bruker MSL NMR Spectrometer and a Heraeus CHN-O Rapid Analyzer, respectively. The molecular weight distributions of the St-BMS copolymers were measured by a Waters Gel Permeation Chromatograph (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 narrow distribution of molecular weights. The thermal properties of the synthesized copolymers were investigated by DSC (TA-Instruments DSC 10) at a heating rate of 10 °C/min in N_2, and TGA (TA- Instruments TGA 51) at a heating rate of 20 °C/min in air or N_2, respectively.

Acknowledgements

The author would like to acknowledge the financial support for this research by the National Science Council, Taiwan, under the contact NSC95-2221- E233-006.

References

[1] Bhaskar, T.; Murai, K.; Matsui, T.; Brebu, M. A.; Uddin, M. A.; Muto, A.; Sakata, Y.; Murata, K. *J. Anal. and Appli. Pyrol.* **2003**, *70*, 369.

[2] Howell, B. A.; Cho, Y. J. *J. Therm. Analy. Calori.* **2006**, *85*, 73.

[3] Motiu, S.; Giurginca, M.; Basus, S.; Petieanu, C. *Materiale Plastice* **1999**, *36*, 221.

[4] Thomas, G. L.; Bohner, C.; Ladlow, M.; Spring, D. R. *Tetrahedron* **2005**, *61*, 12153.

[5] Brebu, M.; Bhaskar, T. Murai, K.; Muto, A.; Sakata, Y.; Uddin, M. A. *Fuel* **2004**, *83*, 2021.

[6] Albrecht, W.; Schauer, J.; Weigel, Th.; Richau, K.; Groth, Th.; Lendlein, A. *J. Membr. Sci.* **2007**, *291*, 10.

[7] Lin, J. S. *Eur. Polym. J.* **2002**, *38*, 79.

[8] Touihri, S.; Bernede, J. C.; Molinie, P.; Legoff, D. *Polymer* **2002**, *43*, 3123.

[9] Ahn, K. D.; Koo, J. S.; Chung, C. M. *J. Polym. Sci. Part A Polym. Chem.* **1996**, *34*, 183.
[10] Chiang, W. Y.; Lu, J. Y. *J. Appl. Polym. Sci.* **1993**, *50*, 1007.
[11] Iijima, T.; Arai, N.; Takematsu, K.; Fukuda, W.; Tomoi, M. *Eur. Polym. J.* **1992**, *28*, 1539.
[12] Iijima, T.; Miura, S.; Fukuda, W.; Tomoi, M. *Eur. Polym. J.* **1993**, *29*, 1103.
[13] Iijima, T.; Hirano, M.; Fukuda, W.; Tomoi, M. *Eur. Polym. J.* **1993**, *29*, 1399.
[14] Matsumoto, A.; Hasegawa, K.; Fukuda, A.; Pae, J. S. *Polym. Int.* **1993**, *31*, 275.
[15] Kim, S. T.; Kim, J. B.; Chung, C. M.; Ahn, K. D. *J. Appl. Polym. Sci.* **1997**, *66*, 2507.
[16] Ahn, K. D.; Koo, D. I.; Willson, C. G. *Polymer* **1995**, *36*, 2621.
[17] Ahn, K. D.; Chung, C. M.; Jo, H. S.; Rhee, J. M. *Polym. Int.* **1998**, *47*, 407.
[18] Chiang, W. Y.; Lin, Y. C. *J. Appl. Polym. Sci.* **2002**, *83*, 2791.
[19] Chiang, W. Y.; Lee, M. L. *J. Appl. Polym. Sci.* **2003**, *90*, 1032.
[20] Shan, G. R.; Weng, Z. X.; Huang, Z. M.; Pan, Z. R. *J. Appl. Polym. Sci.* **1997**, *63*, 1535.
[21] Park, K. H.; Lim, J. T.; Song, S.; Kwak,M. G.; Lee, C. J.; Kim, N. *React. Funct. Polym.* **1999**, *40*, 169.
[22] Suwier, D. R.; Teerenstra, M. N.; Vanhaecht, B.; Koning, C. E. *J. Polym. Sci. Part A: Polym. Chem.* **2000**, *38*, 3558.
[23] Seiner, J. A.; Litt, M. *Macromolecules* **1971**, *4*, 308.
[24] Cais, R. E.; Farmer, R. G.; Hill, D. J. T.; O'Donnell, J. H. *Macromolecules* **1979**, *12*, 835.
[25] Yoshimura,M.; Shirota,Y.; Mikawa, H. *Am. Chem. Soc.* **1976**, *17*, 590.
[26] Iwakura, Y.; Toda, F.; Kusugi, M.; Torii, Y. *J. Polym. Sci. Part A-1, Polym. Chem.* **1971**, *9*, 2423.
[27] Shu, W. J. *J. Appl. Polym. Sci.* **2006**, *102*, 3369.
[28] Shu, W. J. *Polym. J.* **2006**, *38*, 897.
[29] Shu, W. J.; Ho, J. C.; Perng, L. H. *Eur. Polym. J.* **2005**, *41*, 149.
[30] Mayo, F. R.; Lewis, F. M. *J. Am. Chem. Soc.* **1944**, *66*, 1594.
[31] Turner, S. R.; Arcus, R. A.; Houle, C. G.; Schleigh, W. R. *Polym. Eng. and Sci.* **1986**, *26*, 1096.
[32] Fineman, M.; Ross, S. D. *J. Polym. Sci.* **1950**, *2*, 259.
[33] Kelen, T.; Tüdos, F. *J. Macromol. Sci. Chem.* **1975**, *A-9*, 1.
[34] Tidwell, P. W.; Mortimer, G. A. *J. Polym. Sci. Part A* **1965**, *3*, 369.
[35]. Fox, T. G. *Bull. Am. Phys. Soc.* **1956**, *1*, 123.
[36] Kwei, T. K. *J. Polym. Sci. : Polym. Lett. Ed.* **1984**, *22*, 307.
[37] Johnston, N. W. *J. Macromol. Sci. Rev. Macromol. Chem.* **1976**, *C14*, 215.
[38] Shu, W. J.; Perng, L. H.; Chin, W. K.; Hsu, C. Y. *J. Macromol. Sci., Pure Appl. Chem.* **2003**, *A40*, 897.