Graft Copolymerization of Polydimethylsiloxane Macromonomers with Isopropenyl-1,3,5-triazines

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ABSTRACT: Polydimethylsiloxane macromonomers (M_1) having various molecular weights were copolymerized with two isopropenyltriazines (M_2), 2-amino-4-anilino- and 4-(*N*-octadecylanilino)-6-isopropenyl-1,3,5-triazine (AAIT and N18), using azobisisobutyronitrile as an initiator in tetrahydrofuran. r_1 decreased from 0.50 to 0.10 and r_2 increased from 1.97 to 6.47 with the molecular weight of macromonomer for AAIT (M_2). Glass transition temperature (T_g) of the graft copolymers consisting of AAIT segments slightly increased with the molecular weight of macromonomer. The second T_g of silicone segment was observed the below -100°C . The degree of lowering of T_g for the graft copolymers of N18 was larger than that of graft copolymers of AAIT with increasing the siloxane content.

KEY WORDS Macromonomer / Graft Copolymer / Isopropenyl-1,3,5-triazine / Monomer Reactivity Ratio / Glass Transition Temperature / Dynamic Coefficient of Friction /

Polydimethylsiloxane is extremely interesting material having excellent properties, for example, water-repellency, easy peeling, lubricity, resistance to heat, resistance to weather, and high oxygen permeability.^{1–3} Particularly, block and/or graft copolymers containing polydimethylsiloxane have functional properties of both polydimethylsiloxane and another polymers.^{4–6} Graft copolymers consisting of macromonomers are very good materials because graft copolymers show the independent behavior of the backbone part and the graft part.

Works on graft copolymers using polydimethylsiloxane macromonomers were reported. Kawakami^{7,8} reported the preparation of siloxane graft copolymers and the effective surface modification of PMMA films by adding small amounts of siloxane graft copolymers. Cameron^{9,10} reported the monomer reactivity

ratio of siloxane macromonomers towards styrene and acrylonitrile. Tsukahara¹¹ reported the effects of thermodynamic repulsive interactions between the polymer reaction species on copolymerization behavior of polydimethylsiloxane macromonomers with methyl methacrylate.

Polymers with amino-*s*-triazine rings are hydrophilic, rigidly, and heat-stable (high glass transition temperature) ones.^{12–14}

In this work the radical copolymerization of polydimethylsiloxane macromonomers with two isopropenyl-1,3,5-triazines, 2-amino-4-anilino and 4-(*N*-octadecylanilino)-6-isopropenyl-1,3,5-triazine (AAIT and N18), was investigated. T_g and the coating surface of poly(triazines-graft-silicone) containing both the rigid triazine and the flexible siloxane grafts are reported.

Scheme 1. Structures of isopropenyl triazines.

EXPERIMENTAL

Materials

Tetrahydrofuran (THF) and dimethyl sulfoxide (DMSO) were purified by the ordinary method and distilled over calcium hydride under nitrogen.

2-Amino-4-anilino-6-isopropenyl-1,3,5-triazine¹³ (AAIT) and 2-Amino-4-(*N*-octadecylanilino)-6-isopropenyl-1,3,5-triazine¹⁴ (N18) were prepared as described in the previous paper. AAIT: yields 87.5%, mp 175°C. Elemental analysis. Found: C, 64.01%; H, 5.74%; N, 30.77%. Calcd: C, 63.42%, H, 5.77%; N, 30.81% for C₁₂H₁₃N₅. N18: yields 74.9%, mp 75°C. Elemental analysis. Found: C, 75.45%, H, 9.93%, N, 14.68%. Calcd: C, 75.11%; H, 10.29%; N, 14.59% for C₃₀H₄₉N₅.

Measurements

Molecular weights of polymers were determined by gel permeation chromatography (GPC) on a TOSOH HLC-803D with G2000H, G3000H, and G5000H TSK gel-columns and/or on a TOSOH HSC-802UR with G3000H8, G2000H8 TSK gel-columns in a differential refractometric detector in THF. The column was calibrated with monodisperse polystyrene standard samples. ¹H NMR spectra were obtained in CDCl₃ with a 200 MHz Varian XL-200 instrument.

T_g was determined by differential scanning calorimetry (DSC) on a Rigaku-Denki DSC-8230 at a heating rate of 20°C min⁻¹.

Dynamic viscoelasticity was measured with a viscoelastic spectrometer VES-F-III (Iwa-

moto Seisakusho Co., Ltd.). The frequency and heating rate were 10 Hz and 2.5°C min⁻¹, respectively.

Dynamic coefficient of friction of coating surface was measured with a surface property tester HEIDON-14 (Shinto Scientific Co., Ltd.) at 23 ± 2°C and 50% RH. The contact head was a stainless sphere (10 mm diameter) and crosshead speed was 150 mm min.⁻¹

Macromonomers

Methacrylate-terminated polydimethylsiloxane macromonomers (MAS) were supplied by Toshiba Silicone Co., Ltd. and Chisso Co., Ltd. Their structures and characterization are shown in Table I. MAS2 was purified by distillation under reduced pressure. MAS15, MAS16, MAS45, MAS68, and MAS133 were purified by washing with a large quantity of methanol and vacuum drying to constant weight. The molecular weights of macromonomers were determined by GPC and ¹H NMR and formed essentially the same. Macromonomers may thus have about one methacrylate end group per one molecule.

Copolymerization

Polydimethylsiloxane macromonomer was copolymerized with isopropenyl-1,3,5-triazine (AAIT or N18) in THF solution with AIBN as an initiator at 60°C. All reaction solutions were homogeneous and transparent in polymerization. The graft copolymer was precipitated in excess *n*-hexane and dried *in vacuo*. Poly(AAIT-graft-MAS68 or MAS133) containing below 40 wt% of AAIT content, and

Table I. Characterization of silicone macromonomers (MAS_{n+1})

Macromonomer	GPC ^a				¹ H NMR	<i>f</i> ^b
	<i>n</i>	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	$\bar{M}_n$	
MAS2	1	—	—	—	268	—
MAS15	14.4	1270	1430	1.12	1230	1.0
MAS16	15.2	1330	1540	1.16	1180	1.1
MAS45	43.6	3430	4010	1.17	3660	0.9
MAS68	67.2	5180	5870	1.13	5760	0.9
MAS133	131.8	9970	11400	1.14	10700	0.9

^a Molecular weight was calculated by using calibration curve of polystyrene standard samples.

^b End functionality was calculated from $f = \bar{M}_n(\text{GPC})/\bar{M}_n(^1\text{H NMR})$.

poly(N18-graft-MAS68 or MAS133) could not be purified because of similarity of solubility of both macromonomers and graft copolymer.

RESULTS AND DISCUSSION

Copolymerization Behavior of Macromonomers

The relationship between the composition of the monomer feeds and that of the graft copolymers, poly(AAIT-graft-MAS), is shown in Figure 1. The monomer reactivity ratios (r_1 , r_2) obtained from the Kelen-Tüdös plots are shown in Table II. r_1 decreased from 0.50 to 0.10 and r_2 was increased from 1.97 to 6.47 with the molecular weights of the macromonomers. These phenomena are in agreement with the copolymerization with silicone macromonomers and styrene or acrylonitrile.^{9,10} The reason of the relative lowering of the reactivity of the macromonomers may be lowering of the compatibility between silicone macromonomers and AAIT with of molecular weight of the macromonomers. The results of the copolymerization of silicone macromonomers and N18 are shown in Figure 2 and Table II. The variation of r_1 and r_2 was similar to the case of copolymerization with AAIT. r_1 decreased from 0.58 to 0.30 and r_2 increased

Figure 1. Monomer-copolymer composition curves for the copolymerization of AAIT (M_2) with MAS2 (○), MAS15 (●), MAS45 (□), MAS68 (△), and MAS133 (▲) in THF.

from 0.49 to 1.09 with the molecular weights of the macromonomers. The value of $1/r_2$, i.e., the relative reactivity of macromonomers, decreased with increase of the molecular weights. By comparison with AAIT and N18, the relative reactivity of AAIT was fairly higher than that of N18.

The solubilities of silicone macromonomer, poly(AAIT), and poly(N18) were tested.

Table II. Monomer reactivity ratios for the copolymerization of isopropenyl triazines with silicone macromonomers^a

M ₂	M ₁	r ₁ ^b	r ₂ ^b	1/r ₂
AAIT	BuMA ^c	0.45	1.27	0.79
	MAS2	0.50	1.97	0.51
	MAS15	0.19	3.94	0.25
	MAS45	0.14	4.90	0.20
	MAS68	0.10	6.03	0.17
	MAS133	0.10	6.47	0.15
N18	BuMA ^c	0.58	0.40	2.50
	MAS2	0.62	0.42	2.38
	MAS15	0.30	1.09	0.92
	MAS45	0.04	1.08	0.93

^a Copolymerizations was carried out in THF.^b r_1 and r_2 were calculated from the Kelen-Tüdös plots.^c *n*-Butyl methacrylate. **Figure 2.** Monomer-copolymer composition curves for the copolymerization of N18 (M₂) with MAS2 (○), MAS16 (●), and MAS45 (□) in THF.

Silicone macromonomer was soluble in non-polar solvent such as hexane, benzene, and dioxane, and weak polar solvents such as ether, chloroform, pyridine, and THF, whereas insoluble in dipolar aprotic solvents. Poly(AAIT) was insoluble in non-polar solvents, and soluble in THF and dipolar aprotic solvents. Poly(N18) was well-soluble in weak polar and non-polar solvent rather than in

dipolar aprotic solvents. The solubility of poly(N18) was similar that of silicone macromonomers. A common good solvents for both poly(N18) and silicone macromonomers were THF, chloroform, toluene, and benzene. These results suggest that the decrease of relative reactivity of macromonomers with the increase of the molecular weights is due to differences of solubility of between graft copolymer radicals and macromonomers.

Thermal Behavior

T_g of the poly(AAIT-graft-MAS) and poly(AAIT-co-BuMA) is plotted in Figure 3 against AAIT content of the graft copolymers. *n*-Butyl methacrylate (BuMA) was used as a model compound. T_g of the poly(AAIT-co-BuMA) was observed on a straight line between T_g s of poly(AAIT) and poly(BuMA). T_g of poly(AAIT-graft-MAS2) decreased on the straight line above 20 wt% of AAIT content region and the rapidly decrease in T_g was observed below 20 wt%. T_g of the poly(AAIT-graft-MAS15 or MAS16) slightly decreased above 40 wt% of the AAIT content region and rapidly decreased under 40 wt% of the AAIT content region and rapidly decreased under 40 wt%. T_g above 40 wt% of AAIT was higher than that of poly(AAIT-graft-MAS2 or BuMA). Further, the second T_g peak was observed at about -120°C with rapid decrease of the first T_g . This suggests that poly(AAIT-graft-MAS15 or MAS16) has a phase separation structure. Above 40 wt% of the AAIT content region, continuous phase was poly(-AAIT) and dispersed phase was poly(MAS15 or MAS16). Below 40 wt% of AAIT content region, phase inversion occurred. The continuous phase was poly(MAS15 or MAS16) and dispersed phase was poly(AAIT).

T_g of poly(AAIT-graft-MAS68 or MAS133) containing above 50 wt% of AAIT content region was similar to T_g of poly(AAIT). This indicates that phase separation further proceeded with increase of molecular weights of the macromonomers. The reason for the phase

Figure 3. Relationship between T_g and AAIT content in copolymer of AAIT (M_2 , □) with butyl methacrylate (⊕), MAS2 (○), MAS15 (●), MAS16 (◐), MAS 68 (△), and MAS133 (▲).

separation may be that the compatibility between poly(AAIT) and silicone additionally decrease with increase of molecular weights of macromonomers.

Figure 4 shows the dynamic viscoelastic properties of the poly(AAIT-graft-MAS16) containing 22 wt% of AAIT. From the storage modulus (E'), loss modulus (E''), and tangent delta ($\tan \delta$), poly(AAIT-graft-MAS16) have T_g about -100°C , which is in accordance with DSC measurements.

The relation of T_g and N18 content of poly(N18-graft-MAS) and poly(N18-co-BuMA) is plotted in Figure 5. T_g of the copolymer of N18 with BuMA or MAS2 was observed on the straight line between T_g of the homopolymers. This suggests that these polymers are homogenous. T_g of poly(N18-graft-MAS16)s little decreased above 60 wt% of the N18 content region and decreased with decrease of N18 content region below 60 wt%.

Figure 4. Temperature dependence of the storage modulus (E'), the loss modulus (E''), and tangent delta ($\tan \delta$) for poly(AAIT-graft-MAS16) containing 22 wt% of AAIT.

The second T_g of about -120°C was not observed with increase of MAS16 content. This suggests that phase separation occurred above 60 wt% of N18 contents. The phase would invert to composite included structure below 60 wt% of N18 contents region.

It seems that the difference of T_g variation with AAIT and N18 copolymers arose from micro-phase structures of graft copolymers. Thus, copolymers containing N18 having *N*-octadecyl substituent showed increase of hydrophobic properties. The structures of copolymers were not show micro-phase separation and poly(N18) part was compatible with the silicone part.

Dynamic Coefficient of Friction

To estimate the coating surface of graft copolymer containing silicone, the dynamic coefficient of friction (DCF) of coating surface was measured. The value of DCF versus the number average molecular weight of copolymerized silicone macromonomers is plotted

Figure 5. Relationship between T_g and N18 content in copolymer of N18 (M_2 , □) with butyl methacrylate (⊕), MAS2 (⊖), and MAS16 (●).

in Figures 6 and 7. DCF decreased with increase of silicone content and the molecular weights of macromonomers. The variation of DCF of poly(AAIT-*graft*-MAS) is shown in Figure 6. DCF of the poly(AAIT-*graft*-MAS) for 20 wt% of silicone macromonomer was nearly constant below about 5000 of M_n (MAS68). Above 40 wt% of macromonomers, DCF decreased with increase of molecular weights of macromonomers. DCF of poly(AAIT-*graft*-MAS) containing 60 wt% macromonomers rapidly decreased compared with that of the small molecular weight macromonomer (MAS16).

The variation of DCF of poly(N18-*graft*-MAS) is shown in Figure 7. By comparing with poly(AAIT-*graft*-MAS), the DCF of the poly(N18-*graft*-MAS) was rapidly decreased by introducing a small amount (20 wt%) of macromonomers (MAS16) with relatively short silicone chains.

Figure 6. Dynamic coefficient of friction of poly(AAIT-*graft*-MAS) versus the number average molecular weight of silicone macromonomers: silicone contents of 20 wt% (○), 40 wt% (△), 60 wt% (▲), and 80 wt% (●).

Figure 7. Dynamic coefficient of friction of poly(N18-*graft*-MAS) versus the number average molecular weight of silicone macromonomers: silicone contents of 20 wt% (○), 40 wt% (△), 60 wt% (▲), and 80 wt% (●).

These results indicate that the variation of the coating surface occurs not only by the difference of molecular weights of silicone macromonomers but also by the difference of isopropenyl triazines.

The variation of DCF with the difference of isopropenyl triazines would be attributable to the difference of microstructures of two kinds of graft copolymers. That is, isopropenyl triazines become hydrophobic by the introduction of *N*-octadecyl substituent and had good compatibility to silicone macromonomers. Thus, silicone is dispersed homogeneously in coating films and rapid decrease of the DCF occurs on introducing small amounts of silicone macromonomers.

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