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### Synthesis and Gas Permeability of Cyclotetrasiloxane-Containing Methacrylate Copolymers

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## **SYNTHESIS AND GAS PERMEABILITY OF CYCLOTETRASILOXANE-CONTAINING METHACRYLATE COPOLYMERS†**

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**Key Words:** Random copolymers; Block copolymers; Cyclotetrasiloxane-containing methacrylate; Synthesis; Oxygen gas permeability

### **ABSTRACT**

Synthesis and gas permeability of random and block copolymers of a cyclotetrasiloxane-containing methacrylate have been studied in comparison with those of tris(trimethylsiloxy)silane-containing methacrylate (MTTS) copolymers. Random and block copolymers of 3-(heptamethyl cyclotetrasiloxanyl) propyl methacrylate (HCPM) and methyl methacrylate (MMA) were prepared by radical copolymerization using 2,2'-azobisisobutyronitrile and a poly(azoinitiator), poly(1,6-hexamethylene 4,4'-azobiscyanopentanoate), respectively. Differential scanning calorimetry (DSC) revealed that HCPM-MMA block copolymers exhibited heterogeneous phases, as evidenced by two distinct glass transition temperatures due to poly-HCPM (PHCPM) block and PMMA block, while the single glass transition temperatures in the homogeneous phases in HCPM-MMA random copolymers lowered with HCPM content. The oxygen and nitrogen gas permeability coefficients of HCPM-MMA ran-

†Dedicated to Prof. Otto Vogl on his 65th birthday.

dom copolymer films measured at 23°C were found to steeply increase with HCPM contents, although those of HCPM-MMA block copolymers slightly increased. The permeability coefficients of MTTs-MMA random copolymers prevailed over those of HCPM-MMA random copolymers despite the same four Si atoms, probably because of its free volume effect. Further, the HCPM content dependency on the diffusion and solubility coefficients, and the effect of crosslinking on their gas permeability were also discussed.

## INTRODUCTION

Siloxane-containing methacrylate polymers are of practical interest for gas-permeable materials and surface modifiers. The siloxane chains in polymers usually consist of linear or branched chain groups. For example, methacrylate copolymers having pentamethyldisiloxanyl, tris(trimethylsiloxy)silyl, and tris(pentamethyldisiloxanyl)silyl groups are commercially employed as hard contact lens materials [1, 2]. Relationships between copolymer composition and oxygen permeation characteristics for similar copolymers were intensively studied by Peppas et al. [3–5]. Recently, methacrylate-terminated oligosiloxanes called siloxane macromonomers have come to be used not only as surface modifiers but also as gas-permeable materials [6]. However, the copolymers derived from those macromonomers are known to phase-separate depending on the molecular weights of the siloxane chains in the macromonomers [7, 8].

Kawakami et al. reported the effects of incorporating oligomeric dimethyl siloxanes into polymers and their blends on gas permeation properties to obtain high permselectivity by modification of their surface and bulk characteristics [9]. Their intensive study was focused on the synthesis and oxygen gas permeability of oligosiloxane-substituted polystyrenes which form homogeneous phases used to prepare oxygen permselective membranes with high permeability coefficients [10–14]. McGrath et al. emphasized the importance of surface, interface, and bulk morphology contributions in gas transport through multiphase copolymers, i.e., poly(methyl methacrylate)-polydimethylsiloxane graft copolymers and their blends [15, 16]. When relatively low molecular weight polydimethylsiloxane (PDMS) grafts were incorporated, the PDMS grafts were not phase-separated from the poly(methyl methacrylate) (PMMA) matrices and more gas-permeable graft copolymer films were obtained. Those results suggest that the gas permeation technique offers some valuable insight into phase structures of copolymers.

Seno et al. [17] found that tris(trimethylsiloxy)silyl propylglycerol methacrylate copolymer membranes increases oxygen gas permeability as well as surface hydrophilicity. Also, some copolymers of 3-methacryloxypropyltrimethoxysilane modified by transesterification were examined for oxygen gas permeation and surface modification [18].

Methacrylates having cyclic siloxane groups have interesting bifunctional monomers to perform both radical polymerization and ring-opening polymerization, and are thus quite different from unifunctional monomers having linear siloxane groups. However, cyclic siloxane-containing methacrylate copolymers have only been reported in the patent literature [19].

In this work, the preparation of cyclotetrasiloxane-containing methacrylate copolymers, i.e., random and block copolymers of 3-(heptamethyl cyclotetrasiloxanyl)propyl methacrylate (HCPM) with methyl methacrylate (MMA), is studied in detail. The oxygen and nitrogen gas permeabilities of their films cast from chloroform solutions have been evaluated and compared with those of their tris(trimethylsiloxy)silyl-containing analogs, i.e., random and block copolymers of 3-methacryloxypropyl tris(trimethylsiloxy)silane (MTTS), and random copolymers of a methacrylate-terminated oligosiloxane (MOS) (see pp. 418–419).

## EXPERIMENTAL

### Materials

Methyl methacrylate (MMA) was purified by washing with 5% NaOH aqueous solution and water, followed by distillation. 3-Methacryloxypropyl tris(trimethylsiloxy)silane (MTTS, Cisso Co.) was vacuum-distilled. A methacrylate-terminated oligosiloxane was kindly presented by Chisso Co. (CFM 0711,  $M_n = 1000$ , dimethylsiloxy number  $n = 12$ ).

Chloroform as a casting solvent was reagent grade and was used as received. 2,2'-azobisisobutyronitrile (AIBN) was recrystallized from ethanol. A poly(azo-initiator), poly(1,6-hexamethylene 4,4'-azobiscyanopentanoate) (PHMACP\*) was kindly offered by Dr. A. Ueda ( $M_n = 6500$ ,  $M_w = 15,100$ ,  $M_w/M_n = 2.31$ , azo group number = 18).

### Synthesis of 3-(Heptamethyl Cyclotetrasiloxanyl)propyl Methacrylate (HCPM)

In a 500-mL three-necked flask, 8.1 g (40 mmol) heptamethyl cyclotetrasiloxane [20], 100 mL toluene, and a trace of *p-t*-butylcatechol were cooled in an ice-water bath. A few drops of Karstedt catalyst (1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex of platinum) [21] were added slowly and the resulting solution was stirred at room temperature for half a day. Then the toluene was evaporated to concentrate the solution. HCPM was purified by repeated distillation (bp, 98/0.2 torr; yield 20%, gas chromatographic purity 98%; and  $n_D^{20} = 1.4269$ ). The structure of HCPM was identified by  $^1\text{H-NMR}$  and mass spectra (obsd  $m/e = 408$ , calcd  $m/e = 408$ ).

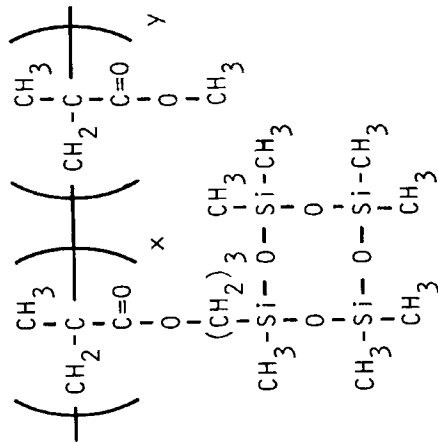
### Synthesis of Random Copolymers (PHCPM-co-MMA, PMTTS-co-MMA, and PMOS-co-MMA)

The random copolymers were prepared by homogeneous copolymerization using 2,2'-azobisisobutyronitrile (AIBN).

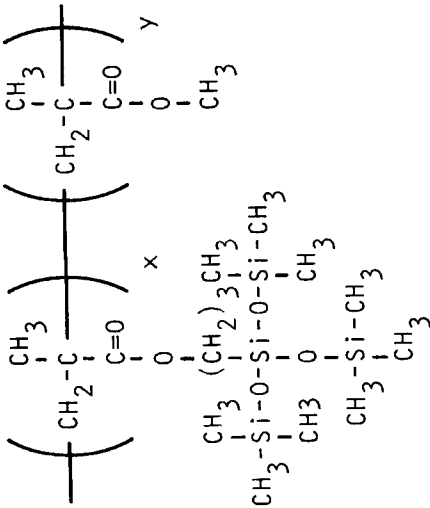
The copolymerization of HCPM and MMA was carried out in sealed tubes. Given amounts of monomers, benzene, and AIBN were put into glass tubes. The air in the tubes was replaced by nitrogen gas by a freezing and thawing technique, followed by sealing under vacuum to make glass ampules.

Polymerization was carried out at 60 or 70°C with shaking. As the polymeriza-

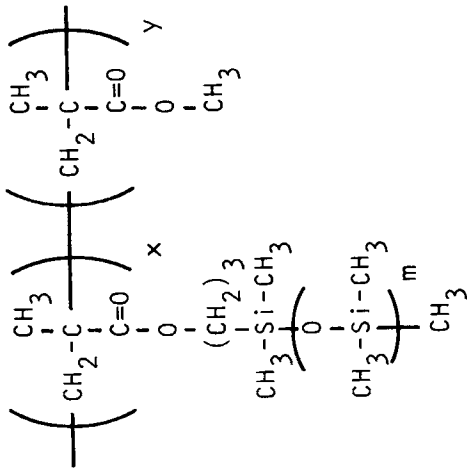
Random Copolymers



(PHCPM-co-MMA)

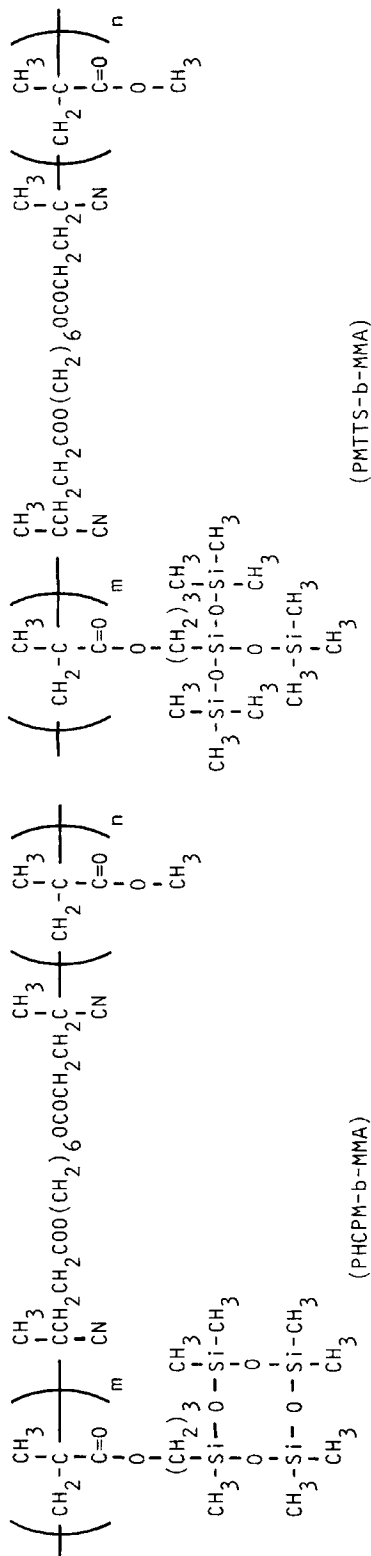


(PMTTS-co-MMA)



(PMOS-co-MMA)

Block Copolymers



tion proceeded, the polymer solution viscosity increased. After reaction for hours, the polymer solution was poured into methanol to precipitate the polymer. The polymers were obtained by filtration with fritted glass filters. The polymers thus prepared were purified by reprecipitation from their chloroform solutions, followed by Soxhlet extraction with petroleum ether.

PMTTS-*co*-MMA and PMOS-*co*-MMA were also prepared by the above-mentioned method.

### Synthesis of Block Copolymers (PHCPM-*b*-MMA and PMTTS-*b*-MMA)

The block copolymers were prepared by a two-step polymerization method using a poly(azo-initiator), poly(1,6-hexamethylene 4,4'-azobiscyanopentanoate) (PHMACP\*) [22].

PHMACP\*/*N,N*-dimethylformamide solution, HCPM, and benzene were put into glass tubes in this order. After replacing the atmosphere in the glass tubes with dry nitrogen, the glass tubes were sealed under vacuum. The ampules were placed in a water bath at 60°C to induce polymerization. After reaction with shaking for 2 h, the ampules were quenched and the polymer solutions were poured into methanol to precipitate the prepolymers still having azo groups. The prepolymers were purified by repeated washing by methanol, and they were finally dried under vacuum at room temperature.

The prepolymer thus obtained were dissolved in MMA and benzene. The resulting solutions were put into glass tubes and sealed. They were shaken in the water bath at 60°C for more than 5 h. The resulting copolymers were separated by precipitation with methanol and purified by reprecipitation with a chloroform-methanol system and Soxhlet extraction with petroleum ether. The block copolymers were dried at 40°C under vacuum.

A similar procedure was applied to synthesize PMTTS-*b*-MMA.

### Preparation of Cast Films

The copolymers were dissolved in chloroform at 5% concentration. The solutions were cast on clean glass plates using a glass applicator and then allowed to stand for almost 2 days. The cast films were detached from the glass plates by immersion in water and dried at 40°C under reduced pressure for more than 2 days. The film thickness ranged from 30 to 60  $\mu\text{m}$ .

### Analysis and Measurements

<sup>1</sup>H-NMR spectra were taken with a JEOL FT-NMR spectrometer FX-90 (90 MHz) using CDCl<sub>3</sub> as a solvent at 50°C to determine the HCPM and MTTTS contents, 100(HCPM)/[(HCPM) + (MMA)] and 100(MTTS)/[(MTTS) + (MMA)], in mol% or wt%.

Molecular weights ( $M_n$  and  $M_w$ ) and their distributions were determined by gel permeation chromatography (GPC) by the use of a Waters liquid chromatograph 150-C (refractive index detector; Shodex columns 80M, 80M and 802.5 in this series; tetrahydrofuran as an eluent at 40°C and 32 bars). The molecular weights were calibrated with 10 polystyrene standards (Pressure Chemicals Co.). Differential

scanning calorimetry (DSC) was performed with a Rigaku DSC-8230B and TAS-100 in a stream of nitrogen at a heating rate of 10°C after it was heated to 160°C and then cooled to -50°C. Glass transition temperatures ( $T_g$ ) were defined as starting points of a change in specific heat.

Oxygen and nitrogen gas permeability coefficients ( $P_{O_2}$  and  $P_{N_2}$ ) were measured with a Toyo Seiki gas permeability measurement instrument M-C3 at 23°C and 50% RH, kept at 800 torr of upstream pressure. Diffusion coefficients ( $D_{O_2}$  and  $D_{N_2}$ ) and solubility coefficients ( $S_{O_2}$  and  $S_{N_2}$ ) were calculated from lag times in the nonsteady-state region based on Henry's law and Fick's law. Separation factors,  $\alpha$ , are defined by the ratios of permeabilities.

$$D = l^2/6t_L$$

$$S = P/D$$

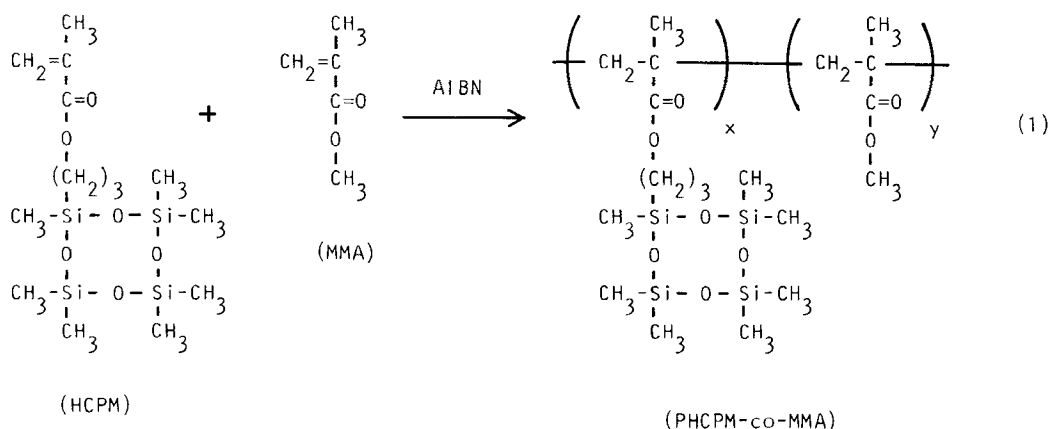
$$\alpha = P_{O_2}/P_{N_2}$$

where  $l$  = film thickness and  $t_L$  = diffusion lag time.

## RESULTS AND DISCUSSION

### Synthesis of Random and Block Copolymers

HCPM-, MTTT-, and MOS-MMA random copolymers (PHCPM-*co*-MMA, PMTTT-*co*-MMA and PMOS-*co*-MMA, respectively) were prepared by conventional radical copolymerization using 2,2-azobisisobutyronitrile (AIBN) (Eq. 1).



The polymerization results for PHCPM-*co*-MMA and PMTTT-*co*-MMA are summarized in Tables 1 and 2, respectively.

These copolymers varied from a solid mass to a colorless viscous oil depending on the monomer composition. The DSC thermograms of the random copolymers indicated only single glass transitions, as shown in Fig. 1. Neither melting nor crystallization transitions similar to block copolymers were detected. The effect of siloxane monomer content on the glass transition temperature ( $T_g$ ) in their copolymers is shown in Fig. 2. Their  $T_g$ 's were found to decrease with the siloxane mono-



TABLE 1. Synthesis of PHCPM-co-MMA

Run	Reactants				Temp. (°C)	Time (h)	Yield (%)	Copolymer (PHCPM-co-MMA)				$T_g$ (°C)	
	HCPM		Benzene					HCPM content		GPC			
	(mmol)	MMA (mmol)	AIBN (mmol)	(mL)				wt%	mol%	$10^{-5}M_n$	$10^{-5}M_w$		$M_w/M_n$
Y86-1	1.2	95	0.30	5	60	1.5	22	3.7	0.9	1.1	1.9	1.67	119
Y86-2	2.5	90	0.30	5	60	1.5	22	8.6	2.3	1.3	2.1	1.62	115
T1.5	0.6	18	0.24	2	60	4.0	90	12.2	3.3	0.23	0.48	2.09	113
Y86-3	4.9	80	0.30	5	60	1.0	23	16.9	4.8	1.2	2.2	1.83	109
T2	1.2	15	0.12	2	60	17.0	98	17.7	5.0	0.47	1.1	2.34	105
T20	12.2	150	2.40	20	70	4.0	86	23.0	6.8	0.23	0.46	2.00	97
Y86-4	7.4	70	0.30	5	60	1.0	18	24.8	7.5	1.3	2.5	1.90	103
Y86-5	9.8	60	0.30	5	60	1.0	22	34.4	11.4	1.5	3.5	2.30	94
T2.5	1.8	13	0.24	2	70	4.0	69	38.7	13.4	0.25	0.51	2.04	81
T3	2.5	10	0.12	2	60	20.0	79	43.8	16.0	0.65	4.3	6.61	73
T4	3.7	5	0.12	2	60	20.0	74	65.5	31.7	0.60	6.6	11.0	39
T5	4.9	0	0.12	2	60	20.0	70	100	100	0.36	1.5	4.17	-31

TABLE 2. Synthesis of PMTTS-co-MMA

Run	Reactants				Temp. (°C)	Time (h)	Yield (%)	Copolymer (PMTTS-co-MMA)				$T_g$ (°C)	
	MTTS (mmol)	MMA (mmol)	AIBN (mmol)	Benzene (mL)				MTTS content		GPC			
								wt%	mol%	$10^{-5}M_n$	$10^{-5}M_w$		$M_w/M_n$
Y141-1	2.4	30	0.12	2	60	4	53	25.3	7.4	1.2	2.8	2.33	101
Y141-2	4.7	20	0.12	2	60	5	61	50.9	19.7	1.7	3.5	2.05	79
Y141-3	5.9	15	0.12	2	60	5	60	62.6	28.4	1.6	3.6	2.25	66
Y141-4	7.1	10	0.12	2	60	5	69	75.8	42.6	1.8	4.2	2.33	47
Y141-5	8.3	5	0.12	2	60	3	60	88.2	63.8	1.9	4.7	2.47	27
Y141-6	4.7	0	0.06	1	60	3	86	100	100	2.9	10.5	3.62	-7

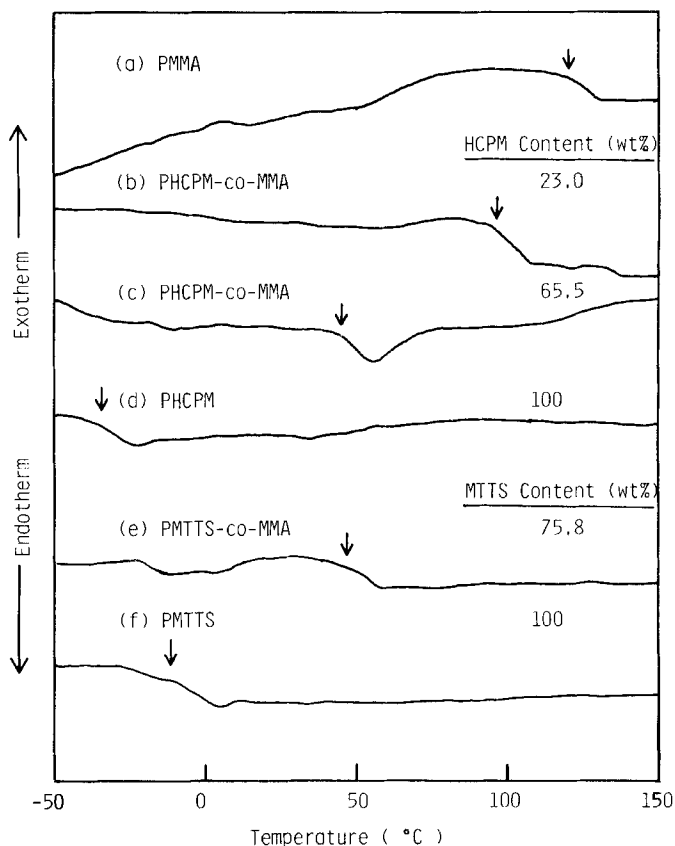


FIG. 1. DSC thermograms of random copolymers (PHCPM-co-MMA and PMTTS-co-MMA). (a) PMMA; (b) PHCPM-co-MMA (T20), HCPM 23.0 wt%; (c) PHCPM-co-MMA (T4), HCPM 65.5 wt%; (d) PHCPM (T5); (e) PMTTS-co-MMA (Y141-5), MTTs 75.8 wt%; (f) PMTTS (Y141-6).

mer content, i.e., HCPM or MTTs content. The  $T_g$ 's for both random copolymers exhibited a positive deviation from the weight averages of the  $T_g$ 's for the two homopolymers. PHCPM had a lower  $T_g$  than PMTTS because the heptamethyl cyclotetrasiloxanyl group is more flexible than the bulky tris(trimethylsiloxy)silyl group in spite of having the same four Si atoms.

All the random copolymer (PHCPM-co-MMA, PMTTS-co-MMA, and PMOS-co-MMA) films prepared by casting from chloroform solutions were found to be transparent, indicative of phase homogeneity. The cast films of random copolymers with siloxane monomer contents below 60 wt%, corresponding to a higher  $T_g$  than room temperature, were subjected to gas permeability experiments.

Synthesis of vinyl-vinyl type block copolymers via a radical mechanism was reported by Ueda et al. [22]. This process is based on two-step polymerizations using a poly(azo-initiator), poly(1,6-hexamethylene 4,4'-azobiscyanopentanoate) (PHMACP\*), in which the asterisk indicates an azo-active polymer. Therefore, sequence regulation and molecular weight control in their block copolymers were

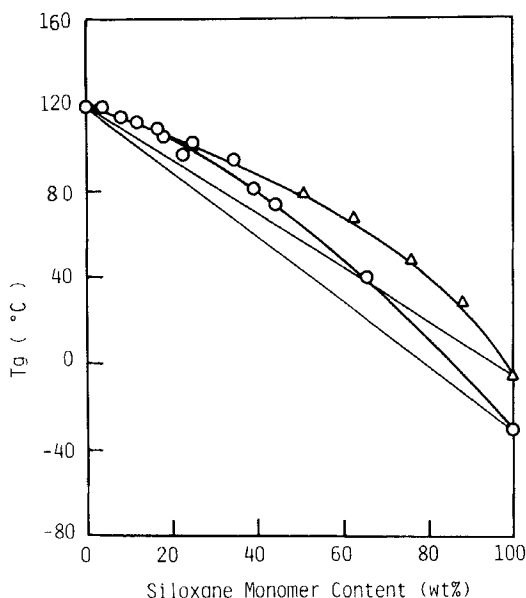


FIG. 2. Glass transition temperatures ( $T_g$ 's) of PHCPM-co-MMA (○) and PMTTS-co-MMA (△).

limited, and their detailed structures were not well-defined compared with those of typical living anionic polymerization processes [23]. This is because of the primary termination of poly(azo-initiator)s, the chain transfer reaction of two termination mechanisms (recombination and disproportionation), and the resulting broad molecular weight distribution [24]. However, the advantage of the poly(azo-initiator) method is easy operation and versatility with radically-polymerizing monomers, allowing us to apply this method for our vinyl-vinyl block copolymer synthesis.

HCPM- and MTTs-MMA block copolymers (PHCPM-*b*-MMA, PMTTS-*b*-MMA, respectively) were prepared by a two-step polymerization technique using PHMACP\* (Eq. 2, see p. 426). In this process the first-step polymerizations of HCPM or MTTs by PHMACP\* (calculated as 18 azo groups in the main chain) at 60°C were stopped in the course of the reaction by quenching to -70°C. The prepolymers (PHCPM\* and PMTTS\*) thus obtained still contained azo groups in their main chains, capable of initiating radical copolymerizations of the second monomers. The purified prepolymers were mixed with the second monomers and allowed to polymerize in a water bath set at 60°C. The polymerization results are summarized in Tables 3 and 4.

The sequence length of PHCPM and PMTTS blocks in their block copolymers cannot be estimated directly from the molecular weights of their prepolymers, PHCPM\* and PMTTS\*. Relatively low initiation efficiency [25, 26] due to primary termination of poly(azo-initiator)s made it hard to determine their block sequence length. Therefore, thermal degradation of their prepolymers, PHCPM\* and PMTTS\*, was examined to estimate the nearly consistent block length. The GPC technique was applied to polymers derived from the thermal degradation of their prepolymers in chloroform in the presence of *t*-butyl catechol at 70°C for 6 h. As can

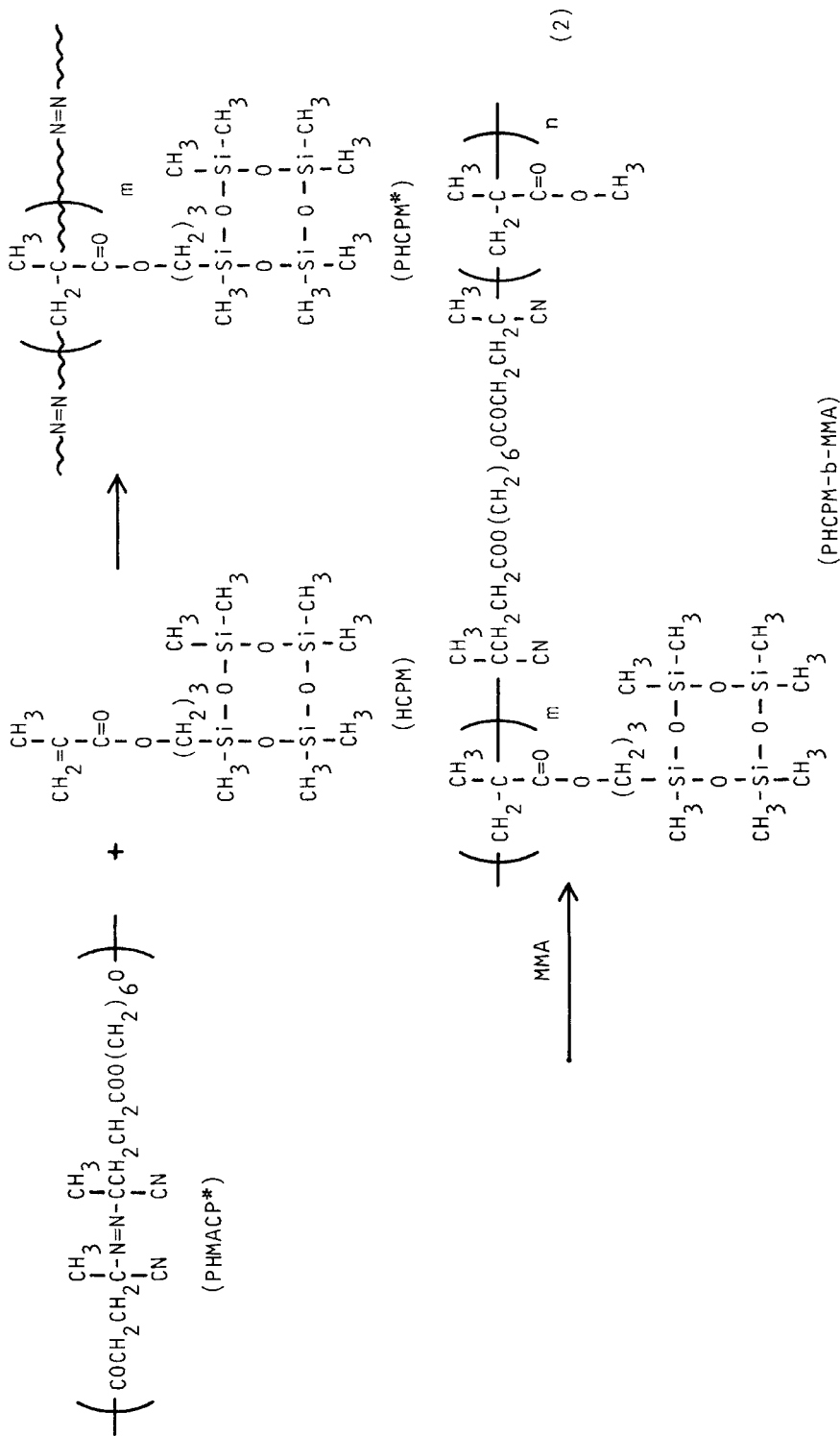


TABLE 3. Synthesis of PHCPM-*b*-MMA

1) First-Step Polymerization														
Reactants		Prepolymer (PHCPM*)				Prepolymer (PHCPM*)								
Run	HCPM (mmol)	PHMACP*		DMF/benzene (mL/mL)	Temp. (°C)	Time (h)	Yield (%)	GPC			GPC (after thermolysis) <sup>b</sup>			
		g	mmol <sup>a</sup>					10 <sup>-5</sup> M <sub>n</sub>	10 <sup>-5</sup> M <sub>w</sub>	M <sub>w</sub> /M <sub>n</sub>	10 <sup>-5</sup> M <sub>n</sub>	10 <sup>-5</sup> M <sub>w</sub>	M <sub>w</sub> /M <sub>n</sub>	10 <sup>-5</sup> M <sub>n</sub>
Y30-8	9.8	0.40	1.10	5/3	60	2	72	0.28	1.3	4.64	0.18	0.81	4.40	
Y173-1	4.9	0.20	0.55	2/1	60	2	65	0.28	1.2	4.28	0.20	0.44	2.27	
Y173-2	7.4	0.30	0.83	3/1	60	2	84	0.40	3.4	8.50	0.17	0.44	2.62	

2) Second-Step Polymerization														
Reactants		Block copolymer (PHCPM- <i>b</i> -MMA)												
Run	PHCPM* No.	g	MMA (mmol)	Benzene (mL)	Temp. (°C)	Time (h)	Yield (%)	HCPM content			GPC			T <sub>g</sub> (°C)
								wt%	mol%	10 <sup>-5</sup> M <sub>n</sub>	10 <sup>-5</sup> M <sub>w</sub>	M <sub>w</sub> /M <sub>n</sub>	10 <sup>-5</sup> M <sub>n</sub>	
Y32-12	Y30-8	2.50	150	5	60	10	90	12.9	3.5	1.2	19	15.8	11	120
Y176-a	Y173-1	1.26	50	3	60	5	93	14.2	3.9	2.1	7.8	3.71	20	114
Y176-b	Y173-2	2.58	50	3	60	5	87	30.5	9.7	2.0	10.5	5.25	11	115

<sup>a</sup>Based on the azo groups.<sup>b</sup>Measured after thermolysis by refluxing for 6 h in CHCl<sub>3</sub> in the presence of *t*-butylcatechol.

TABLE 4. Synthesis of PMTTS-*b*-MMA

1) First-Step Polymerization													
Reactants		PMTTS*					Prepolymer (PMTTS*)						
Run	MTTS (mmol)	PHMACP*		DMF/benzene (mL/mL)	Temp. (°C)	Time (h)	Yield (%)	GPC			GPC (after thermolysis)		
		g	mmol <sup>a</sup>					10 <sup>-5</sup> M <sub>n</sub>	10 <sup>-5</sup> M <sub>w</sub>	M <sub>w</sub> /M <sub>n</sub>	10 <sup>-5</sup> M <sub>n</sub>	10 <sup>-5</sup> M <sub>w</sub>	M <sub>w</sub> /M <sub>n</sub>
Y171-1	7.1	0.30	0.83	3/1	60	2	86	0.36	1.2	3.33	0.44	1.3	2.95
Y174-2	14.2	0.60	1.66	6/1	60	2	87	0.43	1.4	3.26	0.47	3.0	6.38
Y174-3	21.3	0.90	2.49	9/1	60	2	90	0.65	2.1	3.23	0.46	4.2	9.13

2) Second-Step Polymerization														
Reactants		Block copolymer (PMTTS- <i>b</i> -MMA)												
Run	PMTTS* No.	g	MMA (mmol)	Benzene (mL)	Temp. (°C)	Time (h)	Yield (%)	MTTS content			GPC			T <sub>g</sub> (°C)
								wt%	mol%	10 <sup>-5</sup> M <sub>n</sub>	10 <sup>-5</sup> M <sub>w</sub>	M <sub>w</sub> /M <sub>n</sub>	10 <sup>-5</sup> M <sub>n</sub>	
Y176-c	Y174-1	2.40	100	5	60	5	99	21.0	5.9	2.2	12	5.45	31	116
Y176-d	Y174-2	5.58	100	5	60	5	89	35.9	11.7	2.1	12	5.71	21	116
Y176-e	Y174-3	8.75	120	5	60	5	81	47.5	17.6	2.1	14	6.66	24	114

<sup>a</sup>Based on the azo groups.<sup>b</sup>Measured after thermolysis by refluxing for 6 h in CHCl<sub>3</sub> in the presence of *t*-butylcatechol.

be seen from Tables 3 and 4, the molecular weights ( $M_n$ ) of the degraded prepolymers were almost the same or lower than those of the prepolymers. Recombination of the radicals generated from thermolysis of their prepolymers may be a predominant process under these thermolysis conditions, leading to relatively low initiation efficiency. Moreover, considerable amounts of the azo groups in the main chains of PHCPM\* and PMTTS\* are speculated to disappear during first-step polymerization. However, it should be emphasized that such prepolymers are capable of inducing the second polymerization which forms their block copolymers. If the similar conditions are assumed in the second-step polymerization, the PHCPM and PMTTS block lengths are roughly estimated to be less than 17,000–20,000, and 44,000–47,000 for PHCPM-*b*-MMA, PMTTS-*b*-MMA, respectively. On the other hand, PMMA block length was not determined because there was less information on the sequence structures of their block copolymers although AB and ABA (A for PMMA block, and B for PHCPM or PMTTS block) type block copolymers are mainly anticipated. Their block copolymers thus derived were estimated to have a HCPM content of 13–30 wt% for PHCPM-*b*-MMA and a MTTTS content of 20–50 wt% for MTTTS-*b*-MMA by NMR analysis.

Differential scanning calorimetric (DSC) thermograms of their block copolymers are illustrated in Fig. 3. The  $T_g$ 's for their block copolymers were plotted as a function of siloxane monomer content (Fig. 4).

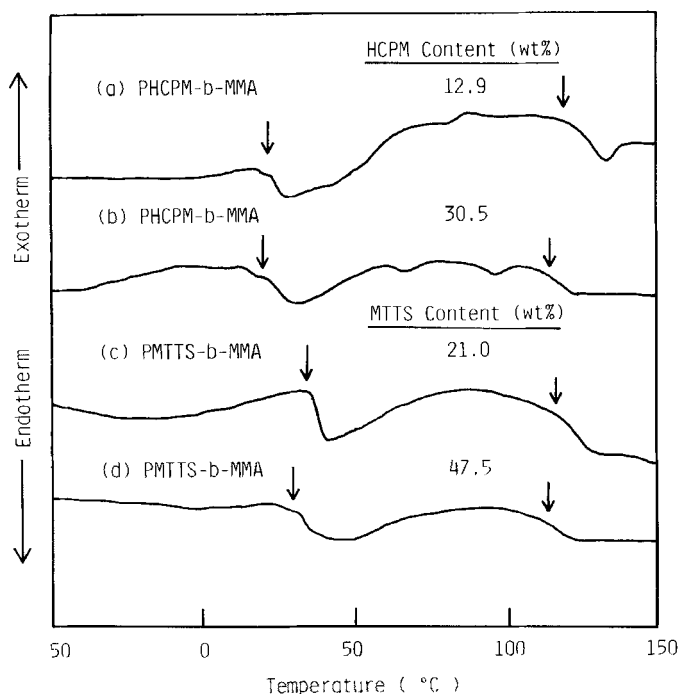


FIG. 3. DSC thermograms of block copolymers (PHCPM-*b*-MMA and PMTTS-*b*-MMA). (a) PHCPM-*b*-MMA (Y32-12), HCPM 12.9 wt%; (b) PHCPM-*b*-MMA (Y176-b), HCPM 30.5 wt%; (c) PMTTS-*b*-MMA (Y176-c), MTTTS 21.0 wt%; (d) PMTTS-*b*-MMA (Y176-e), MTTTS 47.5 wt%.



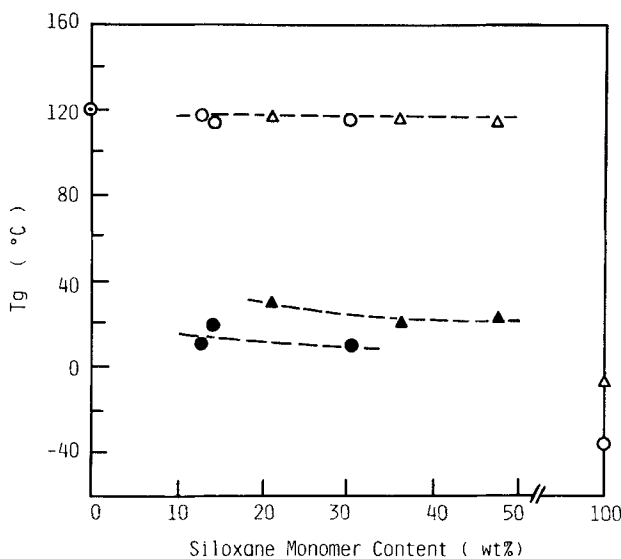


FIG. 4. Glass transition temperatures ( $T_g$ 's) of PHCPM-*b*-MMA and PMTTS-*b*-MMA.

	High $T_g$	Low $T_g$
PHCPM- <i>b</i> -MMA	○	●
PMTTS- <i>b</i> -MMA	△	▲

These figures indicate two distinct glass transitions at 10–20 and 110–120°C for PHCPM-*b*-MMA and at 20–30 and 114–116°C for PMTTS-*b*-MMA, corresponding to the  $T_g$ 's of PHCPM, PMMA, PMTTS, and PMMA blocks, respectively. That is, PHCPM or PMTTS blocks are immiscible with PMMA blocks to form domain structures. The immiscibility between PHCPM (or PMTTS) blocks and PMMA blocks definitely reflects surface segregation of the siloxane moieties, as reported previously [27]. While their  $T_g$ 's in high temperature regions are almost the same as those of PMMA homopolymer, the  $T_g$ 's of PHCPM and PMTTS blocks in low temperature regions are about 40 and 25°C higher than those of the respective homopolymers. This may be attributed to lower molecular weight in PHCPM and PMTTS blocks than their homopolymers, and/or specific interaction between PHCPM (or PMTTS) blocks and PMMA blocks. However, further study is necessary to clarify this phenomenon.

The films for the gas permeability experiments were prepared by casting the chloroform solutions of these block copolymers on glass plates. The cast films of all the block copolymers thus obtained were translucent, also suggesting the presence of phase separation structures consisting of PHCPM or PMTTS blocks as domains and PMMA blocks as matrices.

### Oxygen and Nitrogen Gas Permeabilities

Gas permeability experiments were carried out at 23°C and 50% RH. The cast films of PHCPM-*co*-MMA with HCPM contents up to almost 45 wt% and PMTTS-*co*-MMA with MTTTS contents up to almost 75 wt% were examined for measurements of gas permeability ( $P_{O_2}$  and  $P_{N_2}$ ), diffusion ( $D_{O_2}$  and  $D_{N_2}$ ), and solubility coefficients ( $S_{O_2}$  and  $S_{N_2}$ ).

The oxygen and nitrogen permeability coefficients are summarized in Table 5 for PHCPM-*co*-MMA, PMTTS-*co*-MMA films, and plotted against their siloxane monomer contents, i.e., HCPM and MTTTS contents, in Fig. 5 for both random copolymers.

The gas permeability coefficients of both random copolymer films steeply increased with siloxane monomer content. It was noticed that the PHCPM-*co*-MMA films preferentially increase their gas permeabilities compared with those of PHCPM-*co*-MMA films. Incorporation of cyclic oligosiloxane groups into polystyrenes was also reported to result in moderate increases of permeability coefficients compared with those having the same number of silicon atoms as linear substituents [13].

Their diffusion and solubility coefficients are plotted against siloxane monomer contents in Figs. 6 and 7, respectively.

The diffusion step in the permeation process is the predominant factor in controlling permeability coefficients, as evidenced by a comparison of the increase in their diffusion and solubility coefficients. Both the diffusion and solubility coefficients for PMTTS-*co*-MMA films were much larger than those for PHCPM-*co*-MMA films. This phenomenon can be explained in terms of a free volume effect due to a bulky and branched tris(trimethylsiloxy)silyl group. Although the diffusion coefficients of amorphous films are known to be linearly correlated with their cohesive energy density [28], the difference in the cohesive energy density is not significant between heptamethyl cyclotetrasiloxanyl and tris(trimethylsiloxy)silyl groups. Therefore, the difference in the gas permeability between PHCPM-*co*-MMA and PMTTS-*co*-MMA films may be mainly attributed to a free volume effect.

Gas separation factors,  $\alpha(P_{O_2}/P_{N_2})$ , the ratio of gas permeabilities of two pure gases, are also listed in Table 5. The gas separation factors tend to decrease with an increase of siloxane monomer contents in the copolymers.

Table 6 summarizes gas permeability data for the block copolymers (PHCPM-*b*-MMA and PMTTS-*b*-MMA). Plots of the gas permeability coefficient as a function of siloxane monomer content are shown in Fig. 8.

Figure 8 shows only a slight increase in the gas permeability coefficients for both block copolymers was observed despite an increase of siloxane monomer content. This is quite in contrast with the random copolymers, i.e., PHCPM-*co*-MMA and PMTTS-*co*-MMA. Figures 9 and 10 show diffusion and solubility coefficients of oxygen and nitrogen gases for the block copolymer films. These figures also indicate no significant increase in either coefficient, as expected.

These results evidently reveal low gas permeabilities in block copolymers having phase-separated structures in which PHCPM or PMTTS blocks form their domains, but their gas permeation is disturbed by PMMA blocks as matrices with low gas permeabilities. On the contrary, the homogeneous phases in the random

TABLE 5. Gas Permeation Parameters for Random Copolymers (PHCPM-co-MMA and PMTTS-co-MMA)

No.	Copolymer	Siloxane monomer content (wt%)	Oxygen			Nitrogen			$\alpha$ ( $P_{O_2}/P_{N_2}$ )
			$10^{10}P_{O_2}^a$	$10^8D_{O_2}^b$	$10^3S_{O_2}^c$	$10^{10}P_{N_2}^a$	$10^8D_{N_2}^b$	$10^3S_{N_2}^c$	
Y86-0	PMMA	0	0.53	2.6	2.0	0.10	0.76	1.3	5.3
Y86-1	PHCPM-co-MMA	3.7	0.69	3.3	2.1	0.13	0.70	1.8	5.3
Y86-2	"	8.6	0.65	3.0	2.2	0.12	1.1	1.1	5.4
Y86-3	"	16.9	0.88	3.9	2.2	0.15	1.2	1.3	5.9
Y86-4	"	24.8	1.13	4.0	2.8	0.20	1.4	1.5	5.7
Y86-5	"	34.4	1.94	5.0	3.8	0.42	2.2	1.8	4.6
T3	"	43.8	3.54	13	2.8	0.87	5.9	1.5	4.1
Y141-1	PMTTS-co-MMA	25.3	3.18	9.3	3.4	0.69	4.1	1.7	4.6
Y141-2	"	50.9	19.7	28	7.0	5.06	22	2.3	3.9
Y141-3	"	62.6	40.1	50	8.0	13.4	39	3.4	3.0
Y141-4	"	75.8	67.8	100	6.8	20.9	93	2.2	3.2

<sup>a</sup>Unit:  $\text{cm}^3(\text{STP}) \cdot \text{cm}/\text{cm}^2 \cdot \text{s} \cdot \text{cmHg}$ .<sup>b</sup>Unit:  $\text{cm}^2/\text{s}$ .<sup>c</sup>Unit:  $\text{cm}^3(\text{STP})/\text{cm}^3 \cdot \text{cmHg}$ .

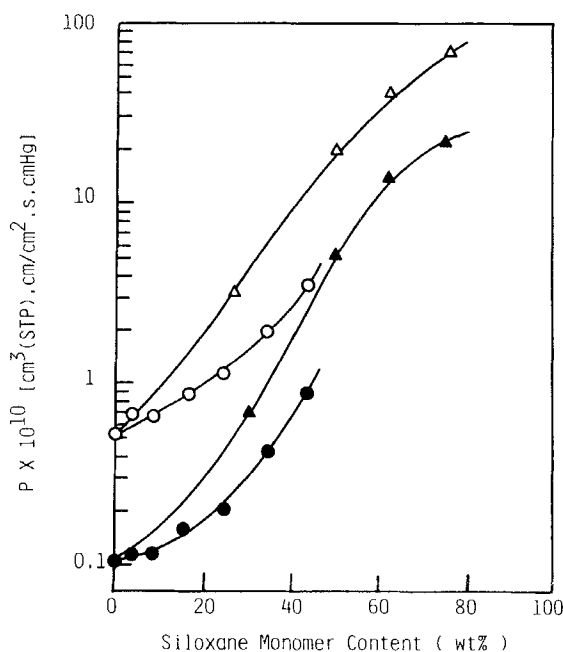


FIG. 5. Oxygen and nitrogen gas permeability coefficients of random copolymer films plotted as a function of siloxane monomer content at 23°C.

	Oxygen	Nitrogen
PHCPM- <i>co</i> -MMA	○	●
PMTTS- <i>co</i> -MMA	△	▲

copolymers can form gas permeation channels by their siloxane substituents. Accordingly, PHCPM-*b*-MMA, and PMTTS-*b*-MMA with PHCPM and PMTTS blocks of lower than 50 wt%, respectively, did not show a steep increase in their gas permeabilities.

Substituted cyclotetrasiloxanes as monomers are already known to react with sulfonic acids to induce ring-opening polymerization [29]. When this reaction was applied to PHCPM-*co*-MMA and PHCPM-*b*-MMA, the crosslinking readily proceeded with heating [30]. The crosslinking of their side chains is expected to affect the gas permeabilities in these copolymers. In this experiment, the random and block copolymers were crosslinked with dodecylbenzenesulfonic acid and were estimated to contain gels of 95–99 and 56–79%, respectively, by solvent extraction.

Figure 11 illustrates the effect of crosslinking on the gas permeability coefficients for PHCPM-*co*-MMA and PHCPM-*b*-MMA.

The oxygen and nitrogen gas permeability coefficients of the crosslinked PHCPM-*co*-MMA films were found to be almost the same as or slightly less than those of the uncrosslinked ones. On the other hand, the gas permeability coefficients for the crosslinked PHCPM-*b*-MMA films decreased to the levels of PMMA homopolymer, although  $P_{O_2}$  and  $P_{N_2}$  for the uncrosslinked block copolymers were origi-

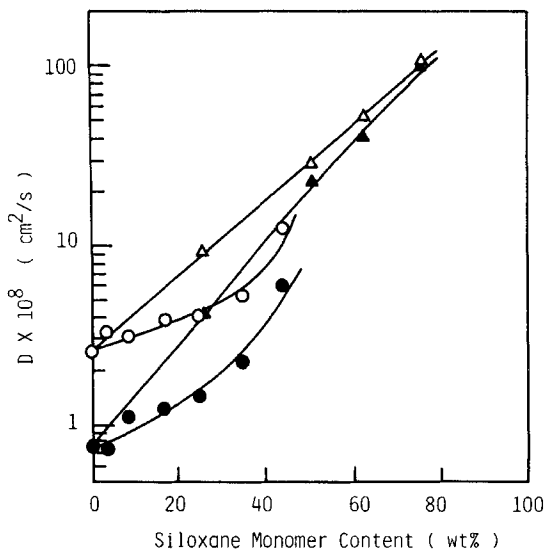


FIG. 6. Oxygen and nitrogen diffusion coefficients for random copolymer films at 23°C.

	Oxygen	Nitrogen
PHCPM- <i>co</i> -MMA	○	●
PMTTS- <i>co</i> -MMA	△	▲

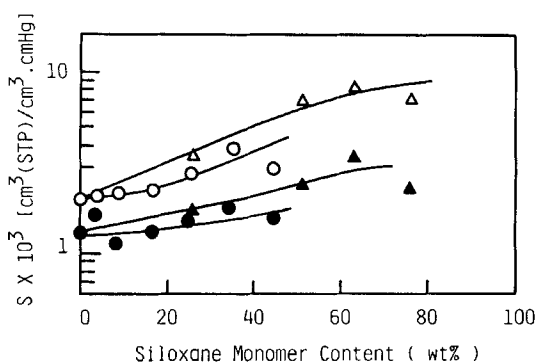


FIG. 7. Oxygen and nitrogen solubility coefficients for random copolymer films at 23°C.

	Oxygen	Nitrogen
PHCPM- <i>co</i> -MMA	○	●
PMTTS- <i>co</i> -MMA	△	▲

TABLE 6. Gas Permeation Parameters for Block Copolymers (PHCPM-*b*-MMA and PMTTS-*b*-MMA)

No.	Copolymer	Siloxane monomer content (wt%)	Oxygen			Nitrogen			$\alpha$ ( $P_{O_2}/P_{N_2}$ )
			$10^{10}P_{O_2}^a$	$10^8D_{O_2}^b$	$10^3S_{O_2}^c$	$10^{10}P_{N_2}^a$	$10^8D_{N_2}^b$	$10^3S_{N_2}^c$	
Y32-12	PHCPM- <i>b</i> -MMA	12.9	0.45	2.1	2.2	0.072	0.62	1.2	6.3
Y176-a	"	14.2	0.60	2.8	2.1	0.11	0.83	1.3	5.5
Y176-b	"	30.5	0.72	3.6	2.0	0.16	1.4	1.1	4.5
Y176-c	PMTTS- <i>b</i> -MMA	21.0	0.52	2.2	2.4	0.083	0.72	1.2	6.3
Y176-d	"	35.9	0.81	3.1	2.6	0.13	1.1	1.2	6.2
Y176-e	"	47.5	0.85	2.8	3.0	0.14	0.86	1.6	6.1

<sup>a</sup>Unit:  $\text{cm}^3(\text{STP}) \cdot \text{cm}/\text{cm}^2 \cdot \text{s} \cdot \text{cmHg}$ .<sup>b</sup>Unit:  $\text{cm}^2/\text{s}$ .<sup>c</sup>Unit:  $\text{cm}^3(\text{STP})/\text{cm}^3 \cdot \text{cmHg}$ .

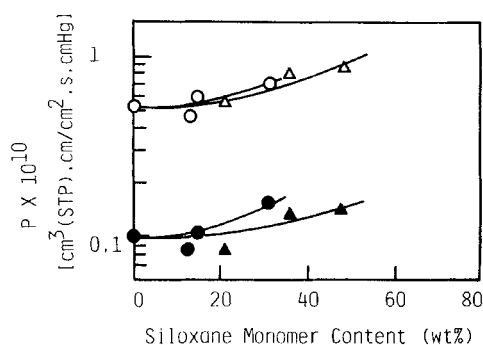


FIG. 8. Oxygen and nitrogen gas permeability coefficients for block copolymer films plotted as a function of siloxane monomer content at 23°C.

	Oxygen	Nitrogen
PHCPM- <i>b</i> -MMA	○	●
PMTTS- <i>b</i> -MMA	△	▲

nally low compared with those for the uncrosslinked PHCPM-*co*-MMA films. For the block copolymers, it can be speculated that only the cyclotetrasiloxane side chains in the domain phase, which are responsible for much of the gas permeation, are ring-opened to form the crosslinked and densed domains, leading to a decrease in their gas permeabilities, while the crosslinking of PHCPM-*co*-MMA brings about a slight volume contraction, resulting in a slight decrease in their gas permeabilities.

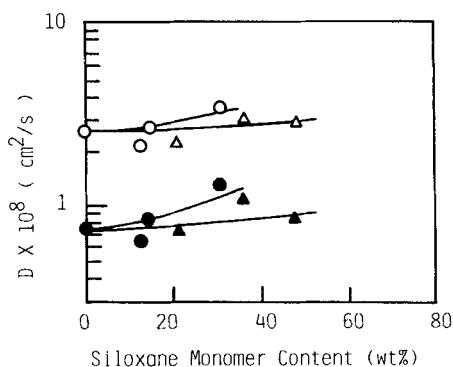


FIG. 9. Oxygen and nitrogen diffusion coefficients for block copolymer films at 23°C.

	Oxygen	Nitrogen
PHCPM- <i>b</i> -MMA	○	●
PMTTS- <i>b</i> -MMA	△	▲

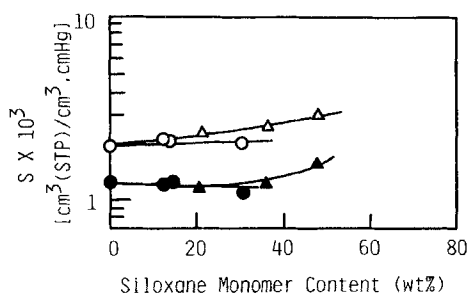


FIG. 10. Oxygen and nitrogen solubility coefficients for block copolymer films at 23°C.

	Oxygen	Nitrogen
PHCPM- <i>b</i> -MMA	○	●
PMTTS- <i>b</i> -MMA	△	▲

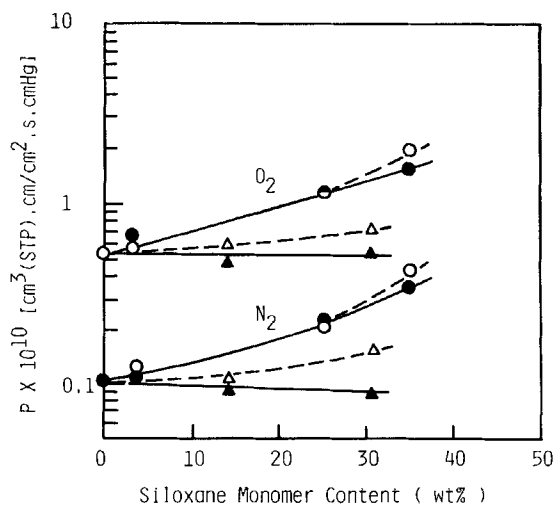


FIG. 11. Effect of crosslinking on permeability coefficients for PHCPM-*co*-MMA and PHCPM-*b*-MMA at 23°C.

	Uncrosslinked		Crosslinked	
	O <sub>2</sub>	N <sub>2</sub>	O <sub>2</sub>	N <sub>2</sub>
PHCPM- <i>co</i> -MMA	○	△	●	▲
HCPM- <i>b</i> -MMA	○	△	●	▲



We also examined gas permeabilities of polymethacrylates containing longer linear siloxane chains, but forming homogeneous phases, in order to compare them with those of PHCPM-*co*-MMA and PMTTS-*co*-MMA with the same siloxane contents. In this experiment a siloxane macromonomer (molecular weight 1000, dimethylsiloxane units  $n = 12$ , MOS) was chosen, although its gas permeation data have been reported [15, 16] and the siloxane contents were corrected on the basis of siloxane weight percentage.

Figure 12 shows oxygen and nitrogen gas permeability coefficients plotted as a function of the corrected siloxane content for PMOS-*co*-MMA, PMTTS-*co*-MMA and PHCPM-*co*-MMA.

This figure indicates that both  $P_{O_2}$  and  $P_{N_2}$  for PMOS-*co*-MMA films are almost the same as or a little bit larger than those for PMTTS-*co*-MMA films in spite of the difference in the siloxane chain length, i.e.,  $n = 4$  and 12. Moreover,

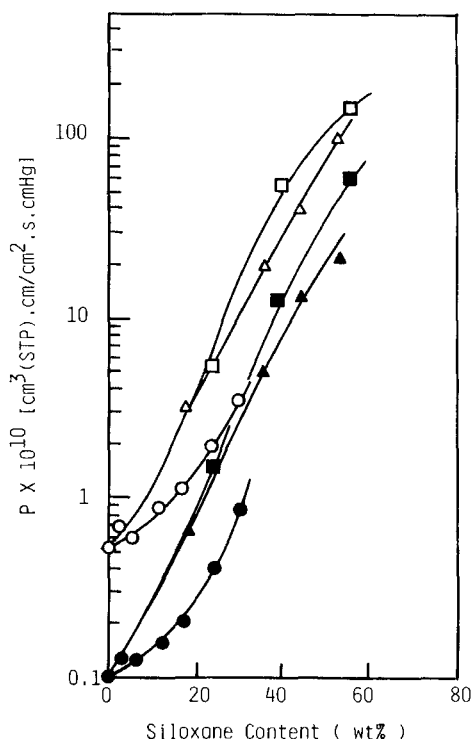


FIG. 12. Comparison of oxygen gas permeability coefficients among random copolymers plotted as a function of the corrected siloxane contents based on the siloxane weight percentage at 23°C.

	Oxygen	Nitrogen
PMOS- <i>co</i> -MMA	□	■
PMTTS- <i>co</i> -MMA	△	▲
PHCPM- <i>co</i> -MMA	○	●

PHCPM-*co*-MMA was confirmed to show lower gas permeability than PMTTS-*co*-MMA and PMOS-*co*-MMA in a region of less than 30 wt% of the corrected siloxane contents. The flexible linear oligosiloxanes chain ( $n = 12$ ) is responsible for high gas permeability because to its free volume effect due to thermal molecular motion.

## CONCLUSION

3-(Heptamethyl cyclotetrasiloxanyl)propyl methacrylate (HCPM) is an interesting monomer with two functions, i.e., radical polymerization and ring-opening polymerization. In this work the synthesis of HCPM-MMA random and block copolymers has easily been performed by the use of radical polymerization techniques. The two-step polymerization methods used to prepare the block copolymers have a limitation in the control of their molecular weights and structures. The single  $T_g$ 's of the random copolymers which form homogeneous phases, PHCPM-*co*-MMA and PMTTS-*co*-MMA, decreased with an increase of HCPM or MTTTS content. On the other hand, the block copolymers were phase-separated, as shown by two distinct  $T_g$ 's attributed to PMMA blocks and PHCPM (or PMTTS) blocks, respectively.

The bulk morphological behavior of these copolymers affected their gas permeabilities. The gas permeability coefficients of PHCPM-*co*-MMA and PMTTS-*co*-MMA films increased steeply with the siloxane monomer content while those of PHCPM-*b*-MMA and PMTTS-*b*-MMA increased slightly in a region of less than 50 wt%. The cyclotetrasiloxanyl groups were found to cause slightly lower gas permeabilities in their random copolymers than tris(trimethylsiloxy)silyl and linear oligosiloxanyl groups. However, it should be emphasized that cyclotetrasiloxane-containing methacrylate copolymers are a group of an interesting functional polymers for gas-permeable materials because of crosslinking that will control other properties.

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