

Bisphenol-A Polycarbonate/Polydimethylsiloxane Multiblock Copolymers. I. Synthesis and Characterization

CHEN-CHI M. MA,¹ JEN-TAU GU,² LIH-HAUR SHAUH,¹ JEN-CHANG YANG,³ WEN-CHEN FANG¹

¹ Institute of Chemical Engineering, National Tsing Hua University, Hsin-Chu, Taiwan, Republic of China

² Catalyst Research Center, China Technical Consultants Inc., Toufen, Miaoli, Taiwan, Republic of China

³ Chemical System Research Division, Chung-Shan Institute of Science and Technology, Lung-Tan, Taiwan, Republic of China

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ABSTRACT: Aminopropyl-terminated polydimethylsiloxane (PDMS)-bisphenol-A polycarbonate block copolymers were synthesized by interfacial phosgenation reaction of 2,2-bis(4-hydroxyphenyl) propane (BPA) and aminopropyl-terminated PDMS. A new synthetic procedure shows better conversion yield of PDMS oligomer. IR, ¹H, ¹³C, and ²⁹Si nuclear magnetic resonance spectra were used to identify the exact chemical structures of the PDMS-PC block copolymers. The conversions of PDMS of these copolymers were ~ 90% and independent of the PDMS content. The intrinsic viscosities, IV, [η] studied were in the range between 0.23 and 2.25 dL/g in dichloromethane at 25°C with different reaction conditions. The intrinsic viscosity and the glass transition temperature decreased with increasing PDMS content at the same reaction temperature, while the melting flow indices increase with increasing PDMS content. Transparent and colorless films, which showed good oxygen-to-nitrogen permselectivity, could be cast from dichloromethane. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **66**: 57–66, 1997

Key words: polycarbonate; polydimethylsiloxane; copolymer; synthesis; characterization

INTRODUCTION

Polycarbonate is a tough, transparent, impact resistant, and widely used engineering thermoplastic resin. However, polycarbonate suffers from its high viscosity when melting. When used in injection molding, the melt viscosity is too high to fill in the thin wall of a mold and its applications are then limited. In order to reduce the melt viscosity

of polycarbonate, combination with cooperating flexible chains, such as siloxane groups, in the rigid molecules of polycarbonate was the main objective of this article. In previous studies, copolymerization with PDMS oligomer was used to improve the thermal stability,¹ flame resistance,² transparency,³ low-temperature impact resistance,⁴ adhesion ability to metal and materials with low surface energy,⁵ and good oxygen-to-nitrogen permselectivity⁶ of polycarbonate.

Since the Si—O—C linkages in polydimethylsiloxane-polycarbonate (PDMS-PC) copolymers are hydrolytically unstable, they would be harmful in its application to biomedical materials; therefore, in Riffle's study,⁷ the Si—O—C linkage was replaced by a Si—C linkage and it was

Correspondence to: Chen-Chi M. Ma.

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found that the hydrolytic resistance could be improved. The PDMS, which was used in this study, was aminopropyl PDMS with a molecular weight of 1000, and its Si—C linkage also may have the advantage of hydrolytic resistance according to Riffle's study.

From previous reports,⁸ by proper selection of optimal reaction parameters such as reaction temperature, BPA solubility in NaOH solution, volume ratio of dichloromethane to water, catalyst, pH value of the aqueous phase, and phosgenation rate, the PDMS-PC block copolymer could be prepared in a short reaction time. The thermal properties, rheology, and permselectivity of the films of PDMS-PC block copolymers were investigated.

EXPERIMENTAL

Materials

The phosgene used was supplied by Matheson Gas Production, U.S.A., with a purity of 99.0%. The aminopropyl PDMS with a weight-average molecular weight of 1000 g/mol and with a viscosity of 20 ± 5 cps, was supplied by the Goldschmidt Pacific Ltd. Co., Germany. The 2,2-bis(4-hydroxyphenyl)propane (BPA), dichloromethane, acetone, and methanol were supplied by the Tokyo Chemical Industry Co., Japan. Triethylamine (TEA) was supplied by the Aldrich Chemical Co., U.S.A. Sodium hydroxide was supplied by the Janssen Chemical Co., Belgium. All reactants and reagents were used as received.

Preparation of Aminopropyl Polydimethylsiloxane (20 wt %)-Polycarbonate Block Copolymers

A freshly prepared solution of bisphenol-A (250 g, 1.10 mol), NaOH (120 g, 3.0 mol), and water (1350 mL) was added to a 5-L reactor. The reactor was equipped with a thermocouple, reflux condenser, phosgene inlet, anchor-type stirrer, and a water-cooling coil. When the solution was cooled to $\sim 30^\circ\text{C}$, dichloromethane (1200 mL) was added to form a two-phase immiscible solution.

The phosgene inlet was then turned on and the phosgene flow was adjusted to a flow rate of 3.2 g/min with vigorous stirring. The reaction temperature was kept at 20°C . When the addition of the phosgene was completed (128 g, 1.29 mol), the pH value of the aqueous phase reached 7,

aminopropyl PDMS (62.5 g, 0.074 mol) was added, and extra phosgene (22 g) was added, forming a slightly viscous fluid. An excess of 50% caustic solution (60 g) was charged into the reactor in order to adjust the pH value of the aqueous phase to $11.5 \sim 12^8$ and triethylamine was added immediately to allow it to polymerize. After stirring for 30 min, a highly viscous, semitransparent fluid was formed in the organic phase indicating that the polymerization was complete. The organic phase was then washed with dilute $\text{NaOH}_{(\text{aq})}$ (6 wt %), then with dilute $\text{HCl}_{(\text{aq})}$ (6 wt %) and with distilled water three times. The polymer was coagulated in a mixed reagent of equal volume of acetone and methanol, and finally dried in an oven at 80°C for 24 h. The yield of the dried copolymer was 330 g at this stage.

The intrinsic viscosity of the copolymer was 1.21 dL/g in dichloromethane, measured at a concentration of 1.0 g/dL at 25°C . The infrared (IR) spectrum of the film of the copolymer showed absorption peaks at 3475 cm^{-1} (N—H), 1778 and 1730 cm^{-1} (C=O), and 1081 cm^{-1} (Si—O—Si). The ^1H -nuclear magnetic resonance (NMR) spectra (CDCl_3) showed peaks at 0.15 ppm (CH_3 in PDMS); 0.6, 1.0, 1.6, and 3.2 ppm (CH_2 in PDMS), 1.65 ppm (CH_3 in PC), 7.0 ppm (H in secondary carbamate), and 7.1–7.3 ppm (aromatic H in BPA). The PDMS conversion calculated from the ^1H -NMR spectra was 95.6%. The ^{29}Si solid-state magnetic resonance spectrum showed peaks at -22 ppm (Si in O—Si—O) and 7.5 ppm (Si in C—Si—O).

Absorbance Analysis

During the phosgenation reaction, a portion of 15 mL of the reaction solution mixture was extracted from the reactor flask every 5 min. The pH value of the aqueous phase of the extracted solution was determined with a pH meter. The concentration of the organic phase was diluted to $\frac{1}{6000}$ of original solution and the absorbance was determined by mixing with an excess amount of *p*-nitrobenzylpyridine (NBP) using a colorimeter, JENWAY PC01, at 470 nm.

Instruments

The ^1H -NMR spectra of the copolymers were recorded on an AM 400 MHz NMR spectrometer, Bruker, Germany. The ^{29}Si -NMR spectra of the

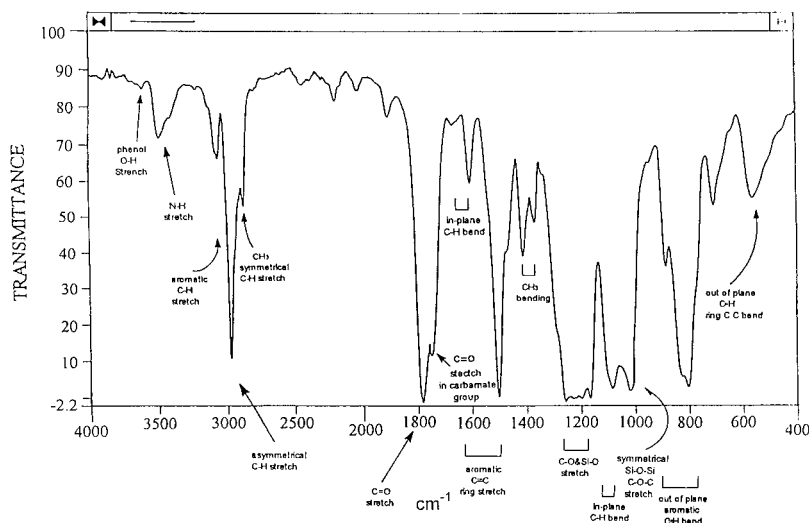


Figure 1 IR spectrum of PDMS-PC copolymer.

copolymers were recorded on a MSL 200 MHz solid state NMR spectrometer, Bruker, Germany. The DSC curves were detected by a Dupont 2000 DSC under nitrogen. The intrinsic viscosities of the copolymers were measured with an Ubbelohde viscometer in dichloromethane at 25°C. The melting flow indices (MFI) of homogeneous polycarbonates and PDMS-PC block copolymers were measured under a load of 2.16 kg at 260°C by a melt-flow indexer. The O₂ to N₂ permselectivity of the films of the PDMS-PC block copolymers were detected by a Yanoco gas permeability analyzer at 25°C and 2 atm. The infrared spectrophotometer used was a Perkin-Elmer IR-842. The thermogravimetric analyzer (TGA) used was a Perkin-Elmer TGS-2.

RESULTS AND DISCUSSION

Synthesis and Identification of the PDMS-PC Block Copolymers

The aminopropyl PDMS-bisphenol-A polycarbonate block copolymers were synthesized with various PDMS contents by a three-step procedure. Initially, from interfacial phosgenation of BPA in caustic solution and dichloromethane, the bischloroformate was formed and dissolved in dichloromethane. In the second step, a desirable amount of aminopropyl PDMS at the pH value of 7 was introduced to react with bischloroformate to form bischloroformate-PDMS carbamate. The amino endgroups of aminopropyl polydimethylsi-

loxane would be a hydrolysis catalyst for chloroformate at high pH value, hence, the pH of phosgenation was kept at 7, then PDMS was added. This carbamate would soon be copolymerized with BPA and other oligomers with OH endgroups through Triethylamine TEA in the final step of reaction in basic solution. The mechanism is illustrated by the following scheme:

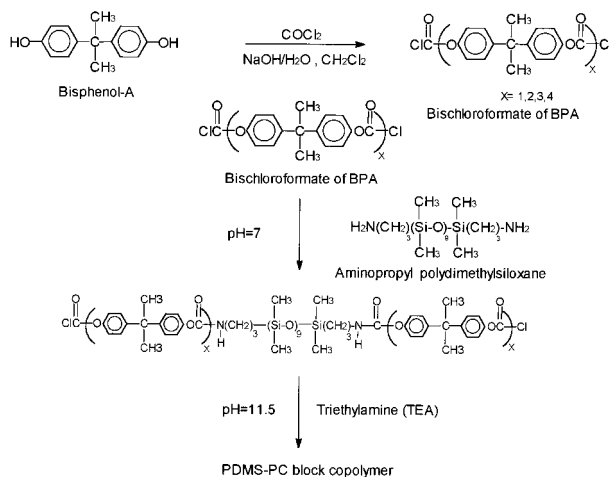


Figure 1 shows the IR spectra of the amino-terminated PDMS-PC copolymer. The N—H stretch vibration of the secondary amide can be seen at 3436 cm⁻¹, which confirms the amino-terminated PDMS was copolymerized with polycarbonate to form copolymer. The absorption peak at 3685 cm⁻¹ is the OH stretch vibration of the phenol group.

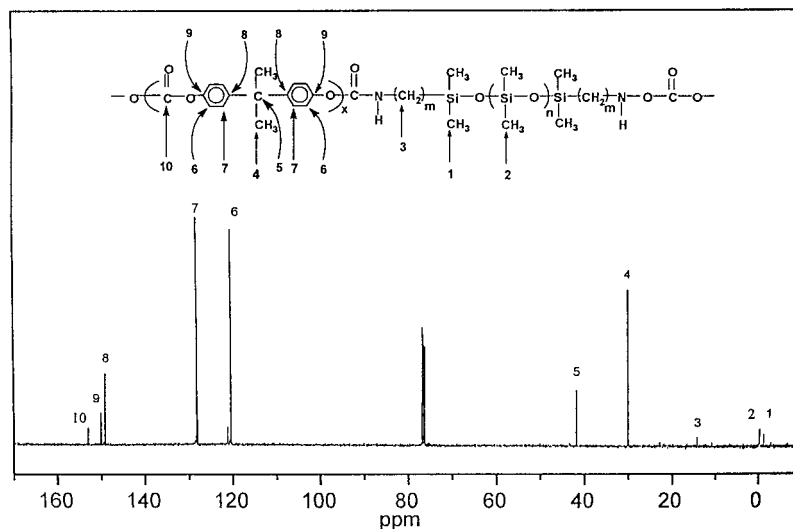


Figure 2 The ^{13}C -NMR spectrum of PDMS-PC copolymer.

The integration of proton in the methyl group of PDMS over the integration of proton in the benzyl group of BPA (the absorption of CDCl_3 was considered) could be used to estimate the mole ratio of PDMS to BPA in copolymer (see Table III). The calculated mole ratio over the designed mole ratio was the PDMS conversion, which ranged from 86 to 96%. Results indicate that this synthetic method was very effective to synthesize the desired product.

Figure 2 shows the ^{13}C -NMR spectrum of amino-terminated PDMS-PC copolymer. The peak at 0 ppm is the carbon absorption of the methyl group in PDMS. The peak at 15 ppm is the carbon absorption of the methylene group. The peak at 31 ppm is the carbon absorption of the methyl group of both ends in the isopropyl group of the PC segment. The peak at 42 ppm is assigned to the quaternary carbon absorption of the isopropyl group. Furthermore, the peaks at 121, 128, 149, and 150 ppm are the benzene ring absorptions in the PC segment. The peak at 154 ppm corresponded to the carbonyl group.

Figure 3 shows the ^{29}Si -NMR spectrum of amino-terminated PDMS-PC copolymer. As can be seen from figure, the peak at -22 ppm is the absorption peak of Si in the $-\text{O}-\text{Si}-\text{O}-$ group and the peak at 7.5 ppm is the absorption peak of Si in the $-\text{C}-\text{Si}-\text{O}-$ group.

The intrinsic viscosities of these copolymers in dichloromethane at 25°C are shown in Table I. Apparently, when the reaction was conducted at 20°C , the PDMS-PC copolymers have higher in-

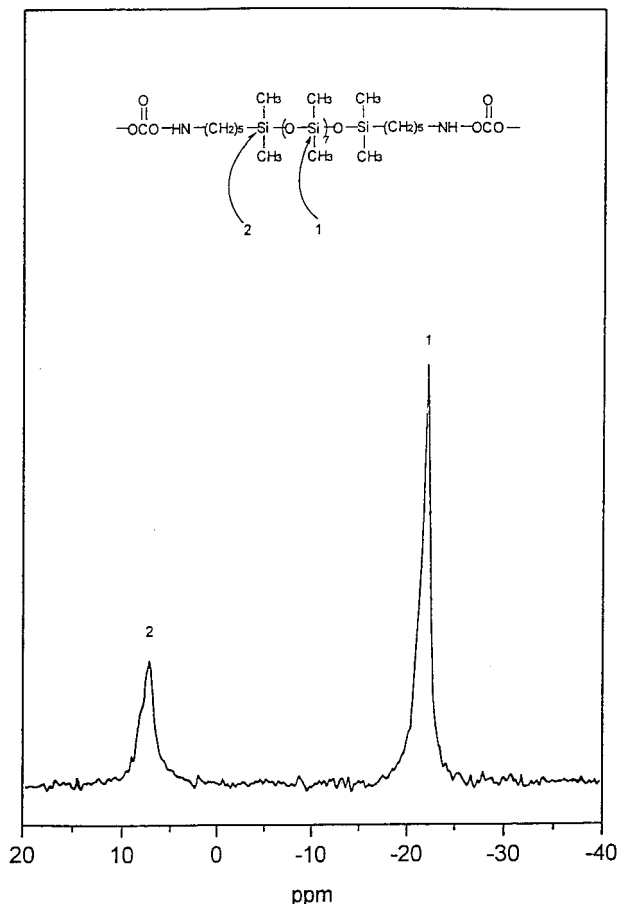


Figure 3 The ^{29}Si -NMR spectrum of PDMS-PC copolymer.

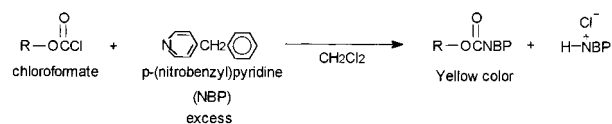
Table I Conversions of PDMS Calculated from Integration of the Peaks on $^1\text{H-NMR}$ Spectrum

Sample Code	Design Mole Ratio	Integration (0.15 ppm)	Integration (7.1–7.3 ppm)	Exact Mole Ratio	Conversion %
25A-20	0.0678	23.14	53.85	0.0623	91.9
25A-25	0.0903	24.62	38.02	0.0863	95.6
25A-30	0.1355	29.56	33.08	0.1160	85.6
25A-40	0.1810	28.53	23.41	0.1625	89.8

trinsic viscosity (IV) than those at 25°C with the same PDMS content. At the same reaction temperature (20°C or 25°C), the IV of the copolymers decreased with increasing PDMS content. This indicates that with more PDMS introduced, more bischloroformate was consumed, consequently, more bischloroformate-PDMS carbamate was formed, also more bischloroformate was hydrolyzed. Consequently, the copolymers formed possess low molecular weight in the shorter blocks of PC.

From Figure 4, it can be seen that the absorbances of chloroformate-NBP at the same phosgenation time at 20°C were higher than when the reaction temperature was at 25°C. This means that, at lower temperature, the hydrolysis of chloroformate and phosgene could be inhibited to some extent. When the rate of phosgenation of monomer was faster than that of hydrolysis of bischloroformate, the absorbance of chloroformate was increased at the beginning of the reaction (0–30 min), so the absorbance of bischloroformate was increased. After 30 min, oligomerization and hydrolysis of bischloroformate were increased,

and the absorbance of chloroformate decreased. But at temperatures <20°C, the bisphenol-A precipitated easily from caustic solution before and during phosgenation. The concentration of the organic phase was diluted to $\frac{1}{6000}$ of origin solution and the absorbance was measured by mixing with an excess amount of NBP using a colorimeter as in a previous report⁹ at 470 nm. The absorbance measured was caused by the adduct product according to the following reaction:



Without adding TEA, the absorbance of the phosgenation product decreased when the pH value was in the range between 12.0 and 11.5. This is due to oligomerization between bisphenol-A bischloroformates, because the hydrolysis of bischloroformate oligomers will increase at high pH (12–13). At a pH value < 11.5, the absorbance

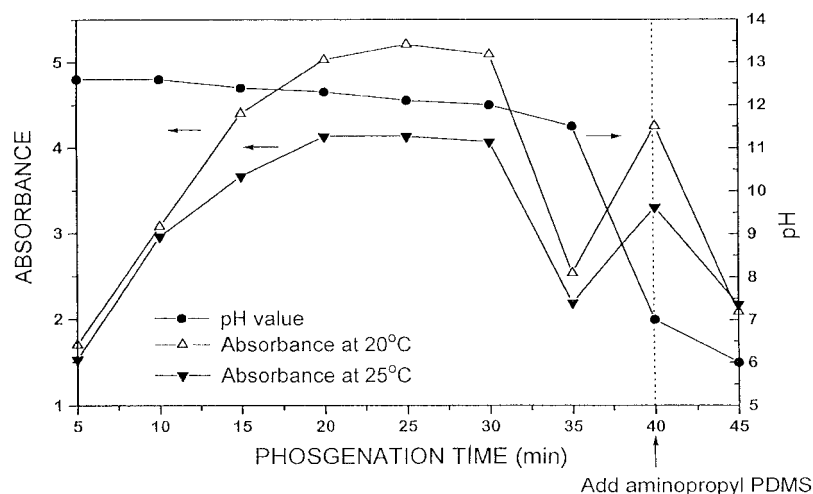


Figure 4 The absorbances of chloroformate-NBP and the pH value during phosgenation at 20°C and 25°C.

Table II Intrinsic Viscosities of PDMS-PC Block Copolymers in CH₂Cl₂ at 25°C

Sample Code	PDMS (wt %)	Intrinsic Viscosity ^a (dL/g)	Sample Code	PDMS wt %	Intrinsic Viscosity ^b (dL/g)
25A-15 ^c	15	0.99	20B-05	5	2.25
25A-20	20	0.94	20B-10	10	1.51
25A-25	25	0.77	20B-15	15	1.35
25A-30	30	0.58	20B-20	20	1.21
25A-40	40	0.23	20B-25	25	1.23
			20B-30	30	1.04
			20B-40	40	0.87

^a The copolymers were synthesized at 25°C.

^b The copolymers were synthesized at 20°C.

^c The meaning of 25A-15 is that the PDMS-PC block copolymer was synthesized at 25°C and there was 15 wt % of PDMS in the copolymer.

increased until the pH value reached 7. At this stage, the aminopropyl DMSO was added to the reacting system; the absorbance and the pH value then decreased to a level which depended on the amount of PDMS added. With more aminopropyl PDMS introduced, more chloroformate was consumed by hydrolysis and polymerization. Consequently, a lower absorbance could be detected with more PDMS added.

The resulting absorbances are summarized in Table II. The delta absorbance versus the amount of PDMS added are illustrated in Figure 5. The delta absorbances are the differences before and after aminopropyl DMSO was added. In summary, a temperature of 20°C may be the lowest temperature limit for this type of interfacial phosgenation, and copolymers with high IV can be easily prepared at this temperature.

Thermal Properties of PDMS-PC Block Copolymers

Figure 6 shows the DSC curves of PDMS-PC copolymer ranging from 50°C to 200°C. The glass transition temperatures of each curve are summarized in Table IV. It is apparent that the glass transition temperature (T_g) decreased with increasing PDMS content, since the block lengths of the PC were decreased. In addition, the IV of the copolymers also decreased with the increasing PDMS content.

The copolymers with PDMS contents 10 wt % showed only one T_g . The copolymers with PDMS contents between 10 and 25 wt % showed two T_g . When the PDMS content exceeded 25 wt %, only one T_g could be found, and the T_g was lowered to 78°C for copolymer with 40 wt % PDMS content.

For all of the PDMS-PC block copolymers which

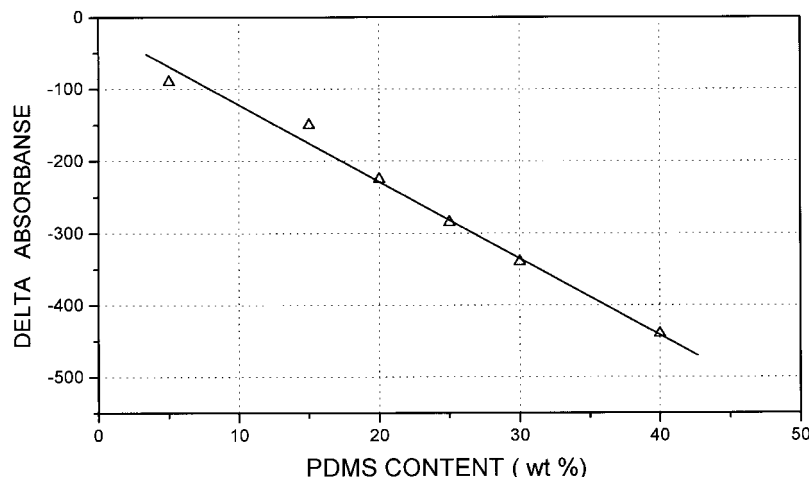


Figure 5 The delta absorbances versus the PDMS content at 20°C. (The delta absorbances were the differences before and after the aminopropyl PDMS were added.)

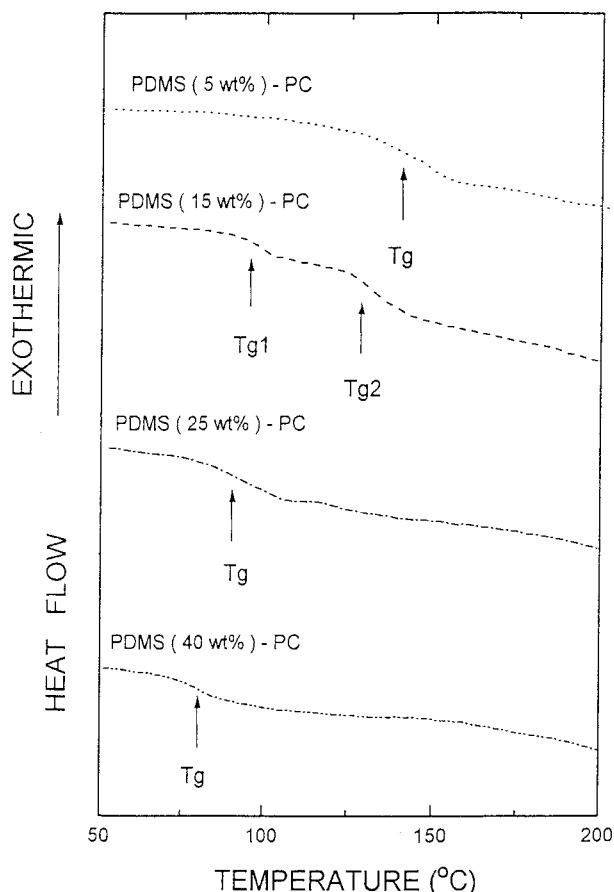


Figure 6 DSC curves of the PDMS-polycarbonate block copolymers with various PDMS contents at a heating rate of 20°C/min in nitrogen.

Table III Effect of Aminopropyl PDMS Content on the Absorbances of the Organic Phase at pH Value of 7 and After Adding Aminopropyl PDMS

PDMS (wt %)	Absorbance ^a (pH = 7)	Absorbance ^b	
		After Adding PDMS	δ Absorbance
5	410	320	-90
15	425	270	-150
20	444	223	-221
25	420	135	-285
30	433	93	-340
40	442	2	-440

^a The absorbance was determined after the extracted concentration was diluted with methylene chloride to 1/6000 of origin at 20°C.

^b The absorbance was determined after adding aminopropyl PDMS at 20°C.

Table IV Thermal Properties of PDMS-Polycarbonate Block Copolymers

Sample Code	PDMS Content (wt %)	T_g 1 ^a (°C)	T_g 2 ^a (°C)	Intrinsic Viscosity (dL/g)
Controlled ^b	0	—	150	0.42
20B-05	5	—	144	2.25
20B-10	10	—	138	1.51
20B-15	15	101	132	1.35
20B-20	20	98	128	1.21
20B-25	25	95	—	1.23
20B-30	30	91	—	1.04
20B-40	40	78	—	0.87

^a Detected at a heating rate of 20°C/min in nitrogen by DSC.

^b The detected homogeneous polycarbonate was Lexan 131 from G.E. Co.

were synthesized in this study, the amounts of monomer (BPA) used were equal; however, the amounts of PDMS were different. It could be concluded that, when the PDMS content was < 10 wt %, there was only the PDMS-poor type of molecule in the copolymers. However, for copolymers with PDMS contents between 10 wt % and 25 wt %, the PDMS-poor type and PDMS-rich type of molecules coexisted. The T_g s of the PDMS-poor type of molecules were higher than the PDMS-rich type molecules, for which phase separation may occur. When PDMS contents exceed 25 wt %, the copolymer had only PDMS-rich molecules.

Figure 7 shows Thermogravimetric Analysis (TGA) curves of the homogeneous polycarbonate (G.E. Lexan 131) and the PDMS-PC block copolymers in air. The homogeneous polycarbonate (G.E. Lexan 131) showed a two-step weight loss. The initial weight loss was due to the decomposition of the carbonate and isopropylene groups.¹⁰ The second step was the decomposition of aromatic rings and there was no residue left at 800°C.

There was a three-step weight loss for the PDMS-PC block copolymers. The initial weight loss started at 300°C, due to the decomposition of propylene and methyl groups on the silicone atoms. The amount of the initial weight loss depended on the PDMS contents. The more the PDMS content, the more initial weight loss measured. The second step was the decomposition of carbonate, carbamate, and isopropylene groups, followed by the final step with weight loss based on the decomposition of aromatic rings. In addi-

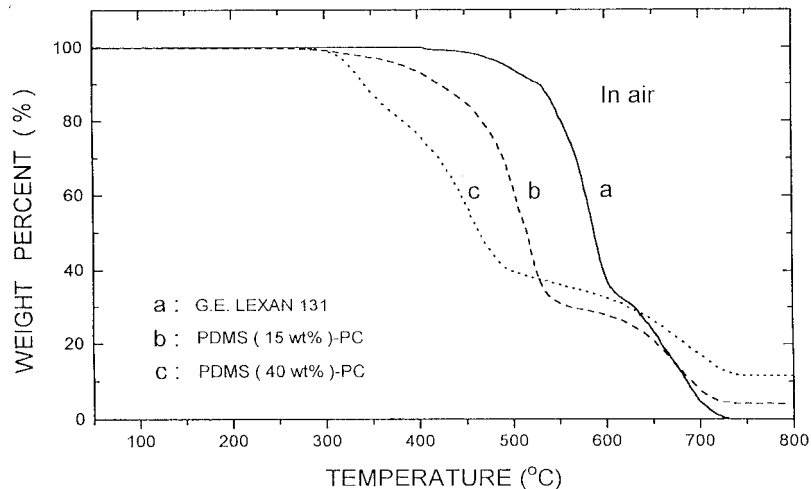


Figure 7 TGA curves of homogeneous polycarbonate (G.E. Lexan 131) and of PDMS-PC block copolymers with various PDMS contents at a heating rate of 20°C/min in air.

tion, the amount of residue after heating to 800°C increased with increasing PDMS content in air.

Figure 8 shows TGA curves of the homogeneous polycarbonate (G.E. Lexan 131) and the PDMS-PC block copolymers under nitrogen. The homogeneous polycarbonate (G.E. Lexan 131) showed a two-step weight loss under nitrogen, first by the decomposition of carbonate groups and second by the decomposition of aromatic rings. There was no residue left at 800°C. There was also a two-step weight loss for the PDMS-PC block copolymers under nitrogen. Here, the initial weight loss was due to decomposition of propylene and methyl

groups on the silicone atoms, followed by the second weight loss that was due to the decomposition of carbonate, carbamate, and isopropylene groups. In addition, the volatile hexamethylcyclotrisiloxane and octamethylcyclotetrasiloxane¹⁰ were also formed in the second weight loss under nitrogen.

Rheology of the PDMS-PC Block Copolymers

The MFI increased linearly with the mole ratio of PDMS to BPA when the PDMS contents were <10 wt %, as shown in Figure 9. It can also be seen

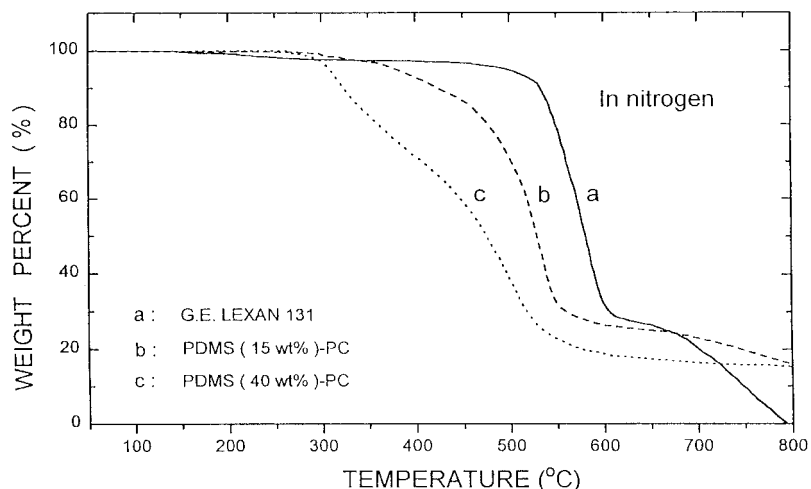


Figure 8 TGA curves of homogeneous polycarbonate (G.E. Lexan 131) and of PDMS-PC block copolymers with various PDMS contents at a heating rate of 20°C/min in nitrogen.

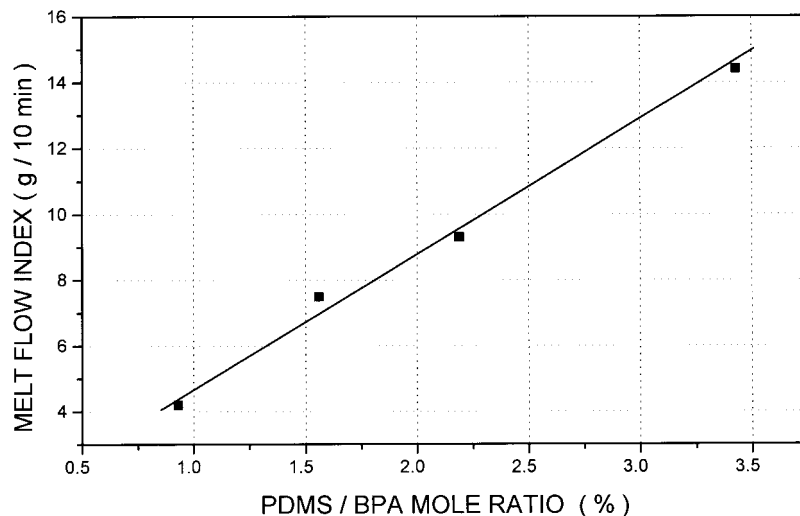


Figure 9 Melt flow indices of the PDMS-polycarbonate block copolymers with various PDMS contents under a load of 2.16 kg at 260°C.

from Table V that the MFI of copolymers containing PDMS were higher than the commercially available PC with similar molecular weight (intrinsic viscosity).

The Permselectivity of Oxygen to Nitrogen of the Thin Films of the PDMS-PC Copolymers

Transparent and colorless films of the PDMS-PC block copolymers could be obtained by casting from dichloromethane solution. The thickness of the films ranged from 10 μm to 1 mm, which could be controlled by the concentration of the dichloromethane solution and the area over which the

solution was spread. Figure 10 illustrates the permselectivity for oxygen to nitrogen of the film (20–30 μm) PDMS-PC copolymer. It shows that the permselectivity ratio of oxygen to nitrogen was <1.0 when the PDMS contents were $<15\%$, and increased significantly from 1.1 for the copolymer with 15 wt % PDMS up to 2.9 for the copolymer with 40 wt % PDMS.

CONCLUSIONS

In order to decrease the melt viscosity of PC and improve the thermal stability, flame resistance,

Table V Comparison of the Melt Flow Indices of the Commercial Products and PDMS-Polycarbonate Block Copolymers

	Sample Code	Intrinsic Viscosity (dL/g)	Melt Flow Index ^a (g/10 min)
PDMS-PC block copolymer	PDMS (3 wt %)-PC		4.2
	PDMS (5 wt %)-PC	2.25	7.5
	PDMS (7 wt %)-PC		9.3
	PDMS (10 wt %)-PC	1.51	14.4
Commercial products	Dow 5		1.7
	Dow 10		4.8
	Dow 15		6.8
	Dow 22		9.4
	G.E. Lexan 131		2.4

^a The melt flow indices were detected under a load of 2.16 kg at 260°C.

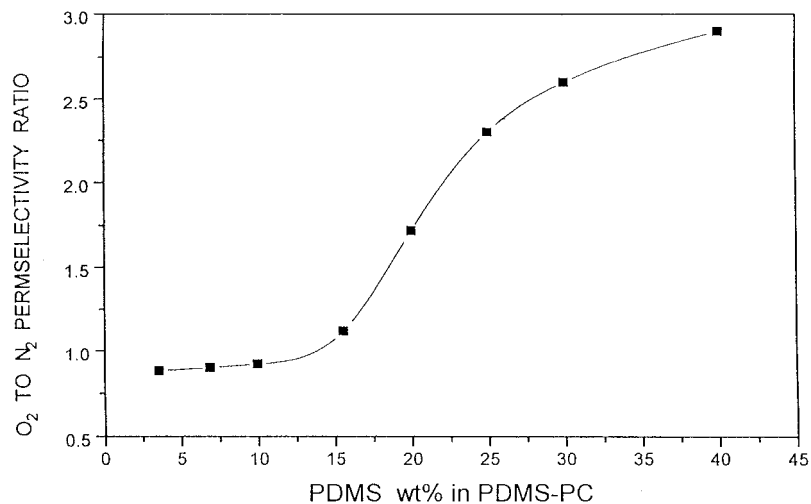


Figure 10 Permeability of oxygen to nitrogen for films of the PDMS-polycarbonate block copolymers with various PDMS contents at 25°C and 2 atm.

and oxygen-to-nitrogen permeability of PC, a new synthetic procedure was proposed which shows better conversion yield of PDMS oligomer. The PDMS-polycarbonate block copolymers have been synthesized by interfacial phosgenation using BPA and aminopropyl polydimethylsiloxane (PDMS) as raw materials. From the synthesis of PDMS-PC copolymer, it was found that aminopropyl PDMS was not only a reactant, but also a hydrolysis catalyst. When phosgenation approached completion, the pH value reached 7, and PDMS oligomer was added to form the PDMS-PC copolymer. The conversion of PDMS-PC copolymer was higher at 90%. The IV of these copolymers were higher with maintaining the reaction temperature at 20°C rather than at 25°C. Moreover, the IV of the copolymers in dichloromethane decreased with increasing PDMS contents at the same reaction temperature. The conversions of the PDMS were ~ 90% for this synthetic method. The viscosity at melt and thermal stability of these copolymers decreased with increasing PDMS content. The permeability selectivity of oxygen to nitrogen for films of the PDMS-PC block

copolymers increased with increasing PDMS content.

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