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STRUCTURAL EFFECTS ON THE THERMAL PROPERTIES OF PDPS/PDMS COPOLYMERS

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A series of PDPS/PDMS copolymers were synthesized through living anionic polymerization with *n*-butyllithium as an initiator. The changes of thermal property as a function of PDPS content were compared with respect to different types of monomer sequence using differential scanning calorimetry and thermogravimtery. The results indicated that the related variations of the thermal properties *vs*. the PDPS content and the monomer sequence provided independent operative control for preparing materials with desired thermal properties. The thermal stability of these copolymers was dramatically improved with introducing PDPS segment. However, the degree of these improvement depended greatly on the monomer sequence in the copolymers.

Keywords: copolymers, polydiphenylsiloxane, polydimethylsiloxane

Introduction

Introduction of diphenylsiloxane segment usually disrupts the low-temperature crystallization of polydimethylsiloxane (PDMS) and also increases the thermal and radiation stability [1]. There has been no systematic study of the structure/property relationship of these novel copolymers.

Reports concerning the thermal stability of PDMS and its copolymers are difficult to compare since the polymers are often not characterized adequately. In particular, the effect of microstructure on copolymer thermal properties has not been adequately studied. The objective of this investigation is to synthesize a series of PDMS/PDPS (polydiphenylsiloxane) copolymers, with similar molecular

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Table 1 The relationships between thermal properties and structures of PDPS/PDMS copolymers

Poly.[a]	$\overline{Mn}$[b]	$\overline{Mw}$ / $\overline{Mn}$	diphenylsiloxy[c] contents /		T_g/°C		T_m[d]/	T_c[d]/	TG[f] / °C		
No.			wt%	mole%	expt.[d]	calc.[e]	°C	°C	T_{10}	T_{50}	T_{80}
Hs-1	40K	1.20	0	0	–123	–123	–41	–	344	377	398
Rb-1	37K	1.37	30	14	–95	–94	–	–	455	512	550
Rb-2	40K	1.34	43	22	–81	–79	–	–	480	530	560
Rb-3	41K	1.41	55	31	–62	–60	–	–	490	550	620
Rb-4	43K	1,40	62	38	–49	–50	–	–	506	560	640[g]
Rs-1	41K	1.42	10	4	–115	–115	–	–	384	426	461
Rs-2	41K	1.40	30	14	–95	–94	–	–	460	513	540
Rs-3	41K	1.30	41	21	–83	–81	–	–	475	535	565
Rs-4	41K	1.38	50	27	–69	–68	–	–	486	553	600
Rs-5	51K	1.46	51	28	–67	–66	–	–	503	553	600
Rs-6	45K	1.43	55	31	–61	–60	–	–	496	560	630
Rs-7	42K	1.42	62	38	–50	–50	–	–	502	560	630[g]
Rs-8	51K	1.39	62	38	–50	–50	–	–	506	560	640[g]
Rs-9	39K	1.29	69	45	–38	–35	–	–	470	508	561
Rs-10	44K	1.43	78	56	–19	–16	–	–	450	488	511
Pb-1	36K	1.40	24	11	–121	–101	–48	–	413	450	487
Pb-2	40K	1.28	30	14	–119	–94	–45	–	423	464	500
Pb-3	43K	1.26	43	22	–112	–79	–	130	432	481	540
Pb-4	44K	1.31	52	29	–112	–70	–	150	443	494	550
Pb-5	45K	1.38	56	32	–	–59	–	160	450	504	544
Pb-6	42K	1.39	63	40	–	–48	–	180	440	500	540
Pb-7	45K	1.44	73	50	–	–25	–	208	420	470	540

Table 1 Continued

Poly.[a]	$\overline{Mn}$[b]	$\overline{Mw}$ / $\overline{Mn}$	diphenylsiloxy[c] contents /		T_g/°C		T_m[d]/	T_c[d]/	TG[f] /°C		
No.			wt%	mole%	expt.[d]	calc.[e]	°C	°C	T_{10}	T_{50}	T_{80}
Ps-1	43K	1.45	31	14	–121	–93	–35	–	421	453	493
Ps-2	40K	1.30	40	20	–119	–82	–48	–	425	480	510
Ps-3	44K	1.40	53	30	–119	–64	–	130	445	493	524
Ps-4	43K	1.38	64	40	–	–46	–	150	438	487	520
Ps-5	43K	1.45	73	50	–	–29	–	167	420	475	517
Ps-6	43K	1.38	82	63	–	–7		196	415	465	527
Bs-1	42K	1.40	15	6	–121	–110	–44	174	350	405	440
Bs-2	40K	1.33	30	14	–122	–94	–45	193	400	450	482
Bs-3	42K*	–	43	23*	–121	–82	–39	215	396	460	490
Bs-4	42K*	–	52	28*	–118	–68	–37	225	400	465	527
Bs-5	42K*	–	57	33*	–119	–57	–38	233	396	469	560
Bs-6	41K*	–	60	36*	–119	–52	–36	241	400	465	523
Bs-7	41K*	–	67	43*	–119	–40	–35	253	400	460	490

(a) *Hs*: Homo PDMS prepared through solution process
Rb, *Rs*: Random copolymer prepared through bulk or solution process
Pb, *Ps*: Pseudo-block copolymer prepared through bulk or solution process
Bs: Block copolymer prepared through solution process
(b) determined by GPC,* estimated from $\overline{Mn}$ of soluble PDMS segment
(c) determined by ^{1}H nmr,* by solid ^{29}Si nmr
(d) determined by DSC
(e) according to Gordon-Taylor equation
(f) determined by TG, T_n: The temperature of *n* wt% loss
(g) The temperature of 70 wt% loss

weight ($\overline{Mn}$ around 40 K) and narrow dispersity, and to correlate their thermal properties with the PDPS content as well as the sequence distribution.

Experimental

Materials

The copolymers were synthesized from hexamethylcyclotrisiloxane (D_3) and hexaphenylcyclotrisiloxane (P_3) in or without proper solvent through anionic polymerization with *n*-butyllithium (*n*-BuLi) as an initiator and diphenylmethylchlorosilane as a terminator. The details of the synthesis methods as well as the characterization of the copolymers were described elsewhere [2]. The chemical compositions, $\overline{Mn}$, and dispersity ($\overline{Mw}$ / $\overline{Mn}$) of the copolymers presented in this paper are summarized in Table1.

Measurements

^{1}H nmr spectra of the copolymers were obtained with a Brucker (300 MHz) spectrometer. Solid ^{29}Si nmr spectra of the non-soluble copolymers were obtained with a Brucker MSL 200 MHz solid state nmr spectrometer. $\overline{Mn}$ and dispersity were measured with a Gel Permeation Chromatography (GPC, Kratos Model Spectroflow 400) using toluene as the eluent and polystyrenes as the standards. Thermogravimetric analysis (TG) and Differential Scanning Calorimetry (DSC) were carried out on DuPont 951 TG analyzer and DuPont 910 DSC, respectively. The heating rate was 10 deg·min^{-1}.

Results and discussion

A series of PDPS/PDMS copolymers with $\overline{Mn}$ around 40 K and narrow dispersity were synthesized from D_3 and P_3 through a living anionic polymerization with *n*-BuLi as an initiator. The copolymers obtained in this way are considered to retain the trimer unit distribution of the starting materials, so that the chemical compositions may be described by $(–Me_2SiO–)_3$ and $(–Ph_2SiO–)_3$ units. The differences in monomer sequencing are shown below, where A = $(–Me_2SiO–)_3$, B = $(–Ph_2SiO–)_3$:

a) Random: (----ABABAABABABBA----) i.e. monomers A and B are randomly spaced along the polymer backbone.

b) Pseudo-block: (----BBBBBBAABABABAAAAAA----) i.e. monomers sequencing in an order of pure B block, mixed AB block, pure A block.

c) Diblock: (----AAAAAAAABBBBBBBB----) i.e. a sharp transition from the A block to the B block.

The different types of copolymers can be made by varying the reaction conditions during the ring opening copolymerization of D_3 and P_3. Random and pseudo-block copolymers were prepared through either bulk or solution process. Diblock copolymers were made by sequentially polymerizing D_3 followed by P_3 through solution process. The Mn of non-soluble solid diblock copolymers (PDPS >20 mole%) was estimated from the Mn of the first polymerized PDMS segment (determined by GPC) and the PDPS wt% of the final copolymer (determined by solid ^{29}Si nmr). Characterization of the copolymers was carried out by ^{1}H nmr, ^{29}Si nmr spectroscopy and differential sequence distribution techniques [2]. The thermal transitions (T_g, T_m, T_c) and the thermal stability of all these copolymers were studied employing DSC and TG techniques. The results were summarized in Table1.

The glass transition temperature (T_g)

Figure 1 shows the T_g's of the PDPS/PDMS random copolymers, in spite of synthesizing through bulk process or solution process, varied with PDPS mole % linearly with a slope of 1.95 and followed Gordon-Taylors equation [3]. The $\overline{Mn}$ of these copolymers were around 40 K. In the literature, the T_g of homo-PDMS was reported to be –123°C and kept almost constant as $\overline{Mn}$ >10 K [4]. The T_g's of PDPS/PDMS random copolymers, $\overline{Mn}$ ranged from 65 to 1500 K, were reported to be a linear function of PDPS mole% as well [5, 6]. For pseudo-block (PDPS content <30 mole%) and diblock copolymers, their T_g's existed around the T_g of homo-PDMS and no significant effect was found by PDPS content. However, the T_g's of pseudo-block copolymers disappeared when the PDPS content >30 mole%. Thus the $\overline{Mn}$ of copolymers has negligible effect on T_g, while the monomer sequencing may vary the T_g drastically.

The melt transition temperature (T_m)

A clearing temperature above 500°C for PDPS/PDMS block copolymer was assigned to be the T_m of PDPS segment [7, 8]. In the present study the maximal operating temperature of DSC was set at 300°C, thus, instead of the T_m of PDPS segment, the T_m's of the PDMS segment in the copolymers would be investigated.

No melt transition of PDMS segment was observed for all the random copolymers. However, it could be observed for pseudo-block copolymers at PDPS content ≤20 mole% and for diblock copolymers at all range of PDPS contents.

Therefore, the low-temperature crystallization of PDMS was disrupted in all of the random copolymers and high PDPS content (>20 mole%) pseudo-block copolymers. For those copolymers which showed this transition, their transition temperature were found to be around that of the homo-PDMS, –41°C. However, the T_m of pseudo-block copolymers was observed for PDPS content ≤25 mole% in a benzene solution copolymerization product by Lee *et al.* [9]. This difference from our result is ascribed to the different fine structure of the mixed AB segment in the copolymer which is controlled by the copolymerization condition.

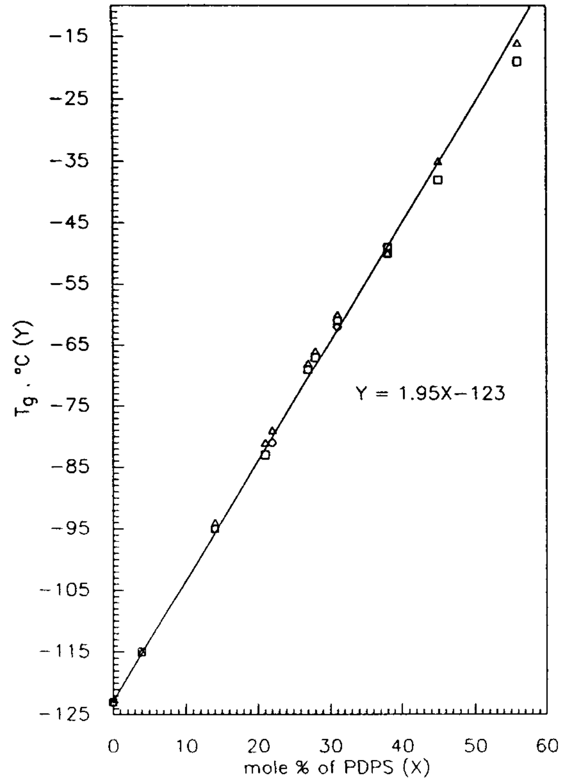

Fig. 1 T_g *vs*. PDPS mole% for PDPS/PDMS random copolymers. o, Random copolymer prepared from bulk process; □, Random copolymer prepared from solution process; Δ, Predict from Gordon-Taylor equation

The crystal to liquid-crystal transition temperature (T_c)

A crystal to liquid-crystal transition was observed for high PDPS content pseudo-block (PDPS >22 mole%) or diblock copolymer, but not for the random copolymers (Table 1). For those copolymers which showed this transition, their T_c's were found to increase linearly with increasing mole% of PDPS in a function of monomer sequencing. From Fig. 2, the following relationships were estimated:

$T_{c_1} = 2.0x + 72$ ------------ For *Ps* series copolymers
$T_{c_2} = 2.8x + 70$ ------------ For *Pb* series copolymers
$T_{c_3} = 2.1x + 163$ ----------- For *Bs* series copolymers

where x = mole% of PDPS

Ps = Pseudo-block copolymer prepared through solution process.
Pb = Pseudo-block copolymer prepared through bulk process.
Bs = Block copolymer prepared through solution process.

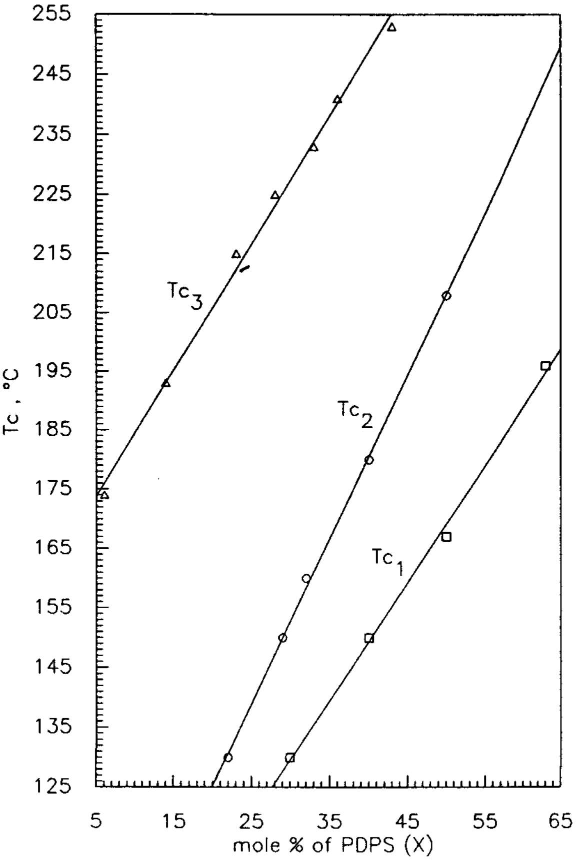

Fig. 2 T_c *vs.* PDPS mole% for PDPS/PDMS copolymers.T_{c1}, Pseudo-block copolymer prepared from solution process; T_{c2}, Pseudo-block copolymer prepared from bulk proces;s T_{c3}, Diblock copolymer prepared from solution process

It suggests that the fine structure of the pseudo-block copolymers prepared through bulk process may be somewhat different from that prepared through solution process. That is because the *Ps* series contains longer mixed AB block and it causes T_c of the copolymer much more affected by PDMS moiety than the *Pb* series did. The lower transition temperature range for the pseudo-block products prepared by solution copolymerization was also supported by Lee's results [9]. For diblock copolymers, this transition appeared at all range of PDPS contents. Their T_c's appeared in a clearly different range as shown in Fig. 2 and coincided with Meier's results [7, 8].

The systematic variance of these transitions also confirms the assignment of the monomer sequencing in the copolymers and can be used as one of the characterization methods for the copolymers.

Thermal stability

General results of thermal analysis were summarized in Table 1. TG of the copolymers in inert atmosphere, showed that the threshold degradation temperature increased with increasing PDPS content and randomness of monomer sequence.

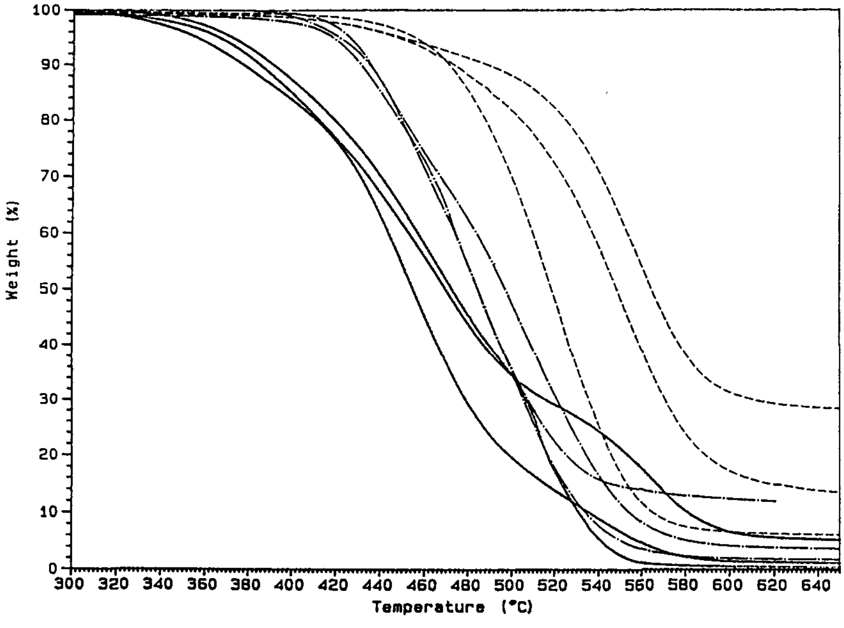

Fig. 3 TG curves in N_2 atmosphere for the copolymers: ----, Random Rs-8, Rs-4, Rb-2; — · —, Pseudo-block, Pb-5, Pb-4, Ps-3; —, Diblock, Bs-5, Bs-4, Bs-3; heating rate: 10 deg·min^{-1}; N_2 flow rate: 100 c.c/min

Figure 3 showed the typical TG profiles of the copolymers. The degradation patterns are apparently classified into different groups with respect to different families of copolymers. As shown in Fig. 4, the thermal stability, as determined by the temperature at 10% weight loss (T_{10}) with TG, of the random copolymers was dramatically improved with increasing PDPS content and reached maximum at 38 mole%. For pseudo-block copolymers, the increment of T_{10} became smaller but also reached maximum at 32 mole% of PDPS content. As for diblock-copolymers, the thermal stability was also improved with increasing PDPS content when it was less than 14 mole% but reached a plateau after that. Thus, the degree of improvement in thermal stability and the thermal degradation patterns greatly depended on the monomer sequence in the copolymers. The mechanism of the thermal degradation is still under investigating in our laboratory.

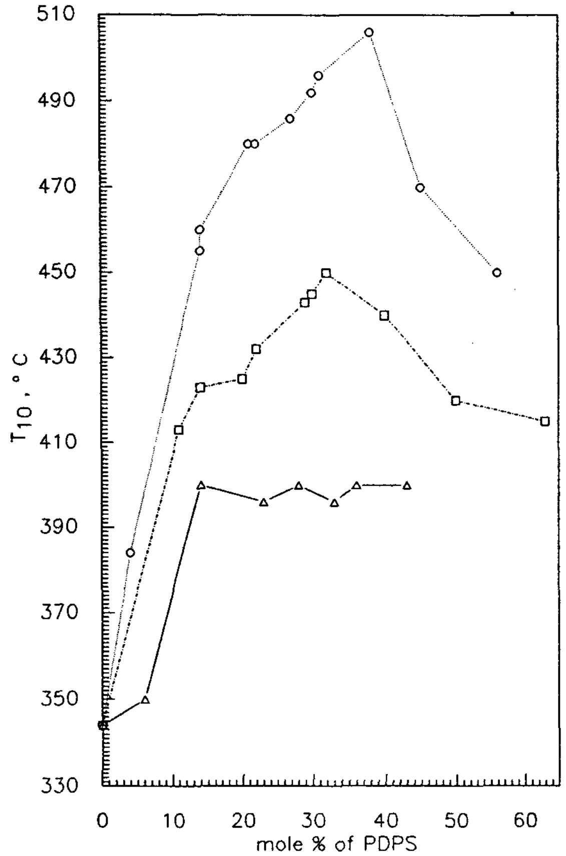

Fig. 4 T_{10} *vs.* PDPS mole% for PDPS/PDMS copolymers o, Random copolymer; □, Pseudo-block copolymer; Δ, Diblock copolymer

Table 2 Summary of property changes as a function of PDPS content and monomer sequence in PDPS/PDMS copolymers

	Random copolymer	Pseudo-block copolymer	Block copolymer
Glass transition temperature (T_g)	1) Increases with wt% according to Gordon-Taylor Eq. 2) Increases linearly with mole%	1) No significant effect 2) Disappeared at PDPS >30 mole%	1) No significant effect 2) Exists at all range
Melt transition temperature (T_m)	Not exist	1) Exists at PDPS <20 mole% 2) Around the T_m of PDMS	1) Exists at all range 2) Around the T_m of PDMS
Crystal to liquid-crystal transition temperature (T_c)	Not exist	1) Exists at PDPS >22 mole% 2) Increases linearly with mole%	1) Exists at all range 2) Increases linearly with mole%
Thermal stability (T_{10} from TG)	1) Increases non-linearly 2) Up to 162°C increase	1) Increases non-linearly 2) Up to 106°C increase	1) Increases non-linearly 2) Up to 56°C increase

Conclusion

Comparison of the thermal properties of a series of PDPS/PDMS copolymers as a function of PDPS content and monomer sequencing was summarized in Table 2. This result provides independent operative control of different thermal properties with different structural variables. For example, if the polymer material was desired to be changed in T_g in the absence of T_c, a random copolymer would be the choice. However, if it was desired to be changed in T_c without a changeable T_g, a pseudo-block or a diblock copolymer would be the choice. Finally, it was found that the low-temperature crystallization of PDMS was disrupted not only in all random copolymers but also in high PDPS content (>30 mole%) pseudo-block copolymers.

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Zusammenfassung — Mittels stöchiometrischer anionischer Polymerisation mit n-Butyllithium als Initiator wurde eine Reihe von PDPS/PDMS Kopolymeren hergestellt. Im Hinblick auf die verschiedenen Arten von Monomersequenzen wurden mittels DSC und TG die Änderungen der thermischen Eigenschaften als eine Funktion des PDPS-Gehaltes untersucht. Die Ergebnisse zeigen, daß die Änderung der thermischen Eigenschaften in Abhängigkeit von PDPS-Gehalt und Monomersequenz eine unabhängige operative Kontrolle zur Herstellung von Materialien mit den gewünschten thermischen Eigenschaften bietet. Die thermische Stabilität dieser Kopolymere wird durch Einbringen von PDPS-Segmenten sehr stark verbessert. Das Ausmaß dieser Verbesserung hängt jedoch stark von der Monomersequenz innerhalb des Kopolymers ab.