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Polymerization and copolymerization behaviour of phenyl-substituted 1,3-disilacyclobutanes

Takuya Ogawa
Research Center, Dow Corning Asia Ltd., Kishi, Yamakita, Kanagawa 258-01, Japan
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Polymerization of two phenyl-substituted 1,3-disilacyclobutanes with or without catalyst was studied for a better understanding of the synthesis of poly(silylenemethylene)s. Copper compounds were found to be effective catalysts for ring-opening polymerization of 1,3-dimethyl-1,3-diphenyl-1,3-disilacyclobutane (**DDDC**) as well as 1,1,3,3-tetraphenyl-1,3-disilacyclobutane regardless of the valence of copper and the counter anion. The catalytic activities of the copper compounds toward polymerization of **DDDC**, however, were found to be quite low compared with platinum or rhodium catalysts. Copolymerization of these two cyclic dimers without catalyst afforded copolymers with $[MePhSiCH_2]/[Ph_2SiCH_2]$ ratios very close to the loaded values. It is suggested from the dimer reactivity ratio that **DDDC** copolymerize with **TPDC** to yield almost random copolymers, while the dimer sequential length distributions in the copolymers are slightly different from an ideal distribution of two dimeric units. © 1998 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

Poly(silylenemethylene)s (**PSMs**) in which the backbone is composed of repeating Si–C units are one of the most well-examined carbosilane polymers, and a number of research activities can be found[1–17].* Although several reports including appreciable contributions by a research group led by Interrante[7–13] dealing with the synthesis of **PSMs** have been published, the thermal and mechanical properties of these polymers have not yet been fully examined. In addition, most **PSMs** reported in the literature have been synthesized by catalytic ring-opening polymerization of 1,3-disilacyclobutanes using platinum compounds because of their high activities toward the cyclic dimers. There are few reports focusing on the polymerization methods using metal catalysts other than Pt. Kriner reported a catalytic activity of various metal species including $PtCl_2$, $IrCl_6^{2-}$, $RuCl_6^{2-}$, $AuCl_4^-$, $PdCl_2$, and RuI_3[2], and Nametkin *et al.* demonstrated the polymerization of (di)silacyclobutanes by metal halides such as $AuCl_3$, $CuCl_2$, and AgCl[5]. Our recent articles reported the synthesis and basic physical properties[19] and the thermal and mechanical properties[20] of the crystalline poly(diarylsilylenemethylene)s (**PDArSMs**) bearing phenyl and tolyl substituents. It was demonstrated in those studies that copper-catalyzed polymerization of corresponding 1,3-disilacyclobutanes was a promising method to prepare **PDArSMs**[19]. We also have reported the synthesis of poly(methylphenylsilylenemethylene) (**PMPSM**) by rhodium-catalyzed polymerization as well as bulk polymerization without catalyst[21].

A catalytic activity of copper compounds toward polymerization of silicon-containing compounds has been reported by Russian researchers using substituted (di)silacyclobutane[5] and dimethylcyclosilazanes[22], although the polymerization mechanism has not been fully discussed. Copper compounds have also been reported to catalyze condensation polymerization reactions, which are dehydrogenative polymerization[23] and dehydrobromination polymerization[24–26] to form silicon-containing polymers. A new synthetic method of poly(silylene)s in which silyl cuprates are used as initiators for ring-opening polymerization of appropriately substituted cyclotetrasilanes was proposed by Matyjaszewski *et al.*[27–29].

In this article, the copper-catalyzed polymerization and copolymerization as well as the non-catalytic copolymerization of two disilacyclobutanes, 1,3-dimethyl-1,3-diphenyl -1,3-disilacyclobutane (**DDDC**) and 1,1,3,3-tetraphenyl-1,3-disilacyclobutane (**TPDC**) are described. Synthesis of block copolymers is of great interest because an improved compatibility between **PMPSM** and poly(diphenylsilylenemethylene) (**PDPSM**) in polymer blends was observed when **PMPSM-PDPSM** block or graft copolymers formed in situ[30,31]. Block copolymerization of **DDDC** and **TPDC** is also discussed.

EXPERIMENTAL

Materials

All liquid solvents are reagent grade and distilled under nitrogen from appropriate drying agents prior to use. Copper compounds and dicumylperoxide are commercially available and were used without further purification. Cyclic dimers for the present study, **DDDC** and **TPDC**, were prepared according to the literature[32]. A pure trans isomer of **DDDC** (^{t}**DDDC**) was isolated from a mixture of cis/trans **DDDC** isomers ($^{c/t}$**DDDC**) by recrystallization[33]. The purity of the $^{c/t}$**DDDC** after vacuum distillation was approximately 98–99% by gas chromatography indicating that some contaminants were present. Although the contaminants could not be identified due to their low contents, potential

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* N. S. Nametkin and co-workers have thoroughly investigated the synthesis and reactions of poly(silalkylene)s. A review article on this has been published [18].

contaminants are some chlorosilanes or hydroxysilanes because chloromethylmethylphenylchlorosilane is an intermediate for synthesis of **DDDC**.

Characterization

Analytical gas chromatography (GC) was performed using a Shimadzu GC-14A gas chromatograph equipped with a DB-5 capillary column (J & W Scientific). ^{1}H, ^{13}C and ^{29}Si n.m.r. spectra were recorded with a Bruker ACP300 spectrometer using tetramethylsilane or 3-trimethylsilyl-1-propanesulfonic acid sodium salt as an internal or external standard, respectively. Gel permeation chromatography (g.p.c.) was performed using chloroform as an eluent with a Tosoh HLC-8020 gel permeation chromatograph equipped with two TSKgel GMHHR-H columns and a refractometer. Average molecular weights and the polydispersities were calculated by the use of polystyrene standards. Differential scanning calorimetry (d.s.c.) was performed using a Perkin Elmer d.s.c. 7/1022 system under a nitrogen atmosphere. Glass transition temperatures (T_gs) of copolymers prepared by quenching the molten samples were obtained from the second heating scan at a heating rate of 20°C/min. Dynamic mechanical properties of copolymers were examined using a Rheometrics RDA II dynamic analyzer in a torsion mode at a constant frequency of 1 Hz. Each specimen ($10 \times 30 \times 1$ mm^3) was prepared by compression moulding at temperatures 50–80°C higher than each T_g for completely amorphous samples and at the temperature 10°C higher than each melting temperature for partially crystalline samples.

Polymer synthesis

Polymerization of ***DDDC*** *using a copper catalyst.* ^{t}**DDDC** (601 mg; 2.2 mmol) was dissolved in 1.5 ml of xylene and heated with CuCl (3.9 mg; 0.039 mmol) at 140°C for 17 h. The brown reaction product was diluted with 3 ml of chloroform and then poured into *ca.* 400 ml of ethanol to yield a polymeric material. Filtration followed by vacuum drying at 80°C gave a colourless solid (420 mg; yield 70%). ^{1}H n.m.r. ($CDCl_3$, ppm): $\delta = -0.1$ (br) and 7.1 (br). ^{13}C n.m.r. ($CDCl_3$, ppm): $\delta = -0.27$, 0.02, 5.9, 6.2, 6.4, 127.7, 128.7, 134.0, and 141.3. ^{29}Si n.m.r. ($CDCl_3$, ppm): $\delta = -4.8$. Molecular weight (M_w by g.p.c.): 35 100. $M_w/M_n = 2.3$.

Polymerization of ***DDDC*** *in the presence of trimethylchlorosilane.* A mixture of ^{t}**DDDC** (161 mg; 0.6 mmol) and trimethylchlorosilane (24 mg; 0.22 mmol) was sealed under reduced pressure while cooling in a liquid N_2 bath then heated at 230°C for 1 h. The product was diluted with 5 ml of chloroform and then poured into *ca.* 400 ml of ethanol to form a polymeric material. Filtration followed by vacuum drying at 80°C yielded a colourless solid (130 mg; yield 81%). ^{1}H n.m.r. ($CDCl_3$, ppm): $\delta = -0.1$ (br) and 7.1 (br). ^{29}Si n.m.r. ($CDCl_3$, ppm): $\delta = -4.8$. M_w by g.p.c.: 269 000. $M_w/M_n = 2.4$.

Copolymerization of ***DDDC*** *and* ***TPDC*** *using a copper catalyst.* A mixture composed of ^{t}**DDDC** (150 mg; 0.56 mmol), **TPDC** (100 mg; 0.26 mmol), and CuCl (1.5 mg; 0.015 mmol) was heated in 0.5 ml of xylene at 140°C for 5 h. A light-yellow solution diluted with 3 ml of xylene underwent the work-up similar to that described above to yield a pale yellow solid (219 mg; yield 88%). ^{1}H n.m.r. ($CDCl_3$, ppm): $\delta = -0.3$ (br, multi) and 7.1 (br, multi). ^{13}C n.m.r. ($CDCl_3$, ppm): $\delta = -1.5$ (br), -0.6, -0.5, -0.1, 2.1 (br), 4.7, 5.0, 5.3, 5.6, 127.6, 128.8, 133.9, 135.7, 138.8, and 141.4. ^{29}Si n.m.r. ($CDCl_3$, ppm): $\delta = -4.8$, -8.8, -9.1, and -9.5. M_w by g.p.c.: 124 000. $M_w/M_n = 2.8$.

Copolymerization of ***DDDC*** *and* ***TPDC*** *without catalyst.* ^{t}**DDDC** (3.0 g; 11.2 mmol) and **TPDC** (2.0 g; 5.1 mmol) were placed in a test-tube, and sealed under reduced pressure. The mixture was first homogenized by heating at 140°C for 5 min and subsequently heated at 300°C for 5 h. After cooling the product was crushed then heated under reflux in 30 ml of ethanol to remove unreacted cyclic dimers. Filtration followed by vacuum drying at 80°C yielded a colourless solid (4.94 g; yield 99%). The product was insoluble in common solvents. ^{29}Si n.m.r. (CP/MAS, ppm): $\delta = -11.7$ and -16.1.

Block copolymerization of ***DDDC*** *and* ***TPDC***. $^{c/t}$**DDDC** with the [cis-**DDDC**]/[trans-**DDDC**] molar ratio of 79/21 (1.0 g; 3.73 mmol) was heated with CuCl (2.4 mg; 0.024 mmol) in xylene (1.2 ml) at 140°C for 6 h. To the solution were added **TPDC** (670 mg; 1.71 mmol) and xylene (5 ml), and was further heated for 15 h. The product underwent centrifugation to separate a xylene-soluble material. A colourless viscous material obtained after the removal of xylene was diluted with 5 ml of chloroform and poured into 500 ml of ethanol. Filtration followed by vacuum drying at 80°C yielded a colourless solid (955 mg; yield 95%). ^{29}Si n.m.r. ($CDCl_3$, ppm): $\delta = -4.7$. M_w by g.p.c.: 46 100. $M_w/M_n = 2.4$.

A xylene-insoluble material obtained as a precipitate was washed with hot ethanol and dried in vacuo to provide a light-yellow solid (255 mg). The product was not soluble in common solvents. ^{29}Si n.m.r. (CP/MAS, ppm): $\delta = -16.1$ and -17.8.

Monitoring the polymerization behaviour of ***DDDC*** *and* ***TPDC*** *by d.s.c.*

Each cyclic dimer (5–8 mg) was placed in an aluminium pan with a catalytic compound (0.3–0.5 mg) and sealed in an ambient atmosphere. Polymerization behaviour of cyclic dimers was monitored by d.s.c. in the first heating scan at a rate of 10°C/min under a nitrogen atmosphere.

RESULTS AND DISCUSSION

Monitoring the polymerization behaviour of ***DDDC*** *and* ***TPDC*** *by d.s.c.*

D.s.c. measurements led to significant understanding of the polymerization behaviour of **DDDC** and **TPDC** in the presence of various catalysts including CuCl, $CuCl_2$, and $Cu(acac)_2$, and dicumylperoxide [$(PhMe_2CO)_2$; **DCP**]. The d.s.c. heating thermograms of three substrates, $^{c/t}$**DDDC**, ^{t}**DDDC**, and **TPDC**, without catalyst are depicted in *Figure 1*. Two endothermic peaks at 139°C and at 350°C on curve *(c)* are assignable to the melting transitions of **TPDC** and **PDPSM**, respectively. The polymerization of each sample is responsible for an exothermic peak in each thermogram. It is of interest that the polymerization temperature of $^{c/t}$**DDDC** is much lower than that of ^{t}**DDDC**. Since the lowering effect by some contaminants in $^{c/t}$**DDDC** is suspected, several experiments were carried out to clarify this issue as will be discussed in the section below.

The d.s.c. heating thermograms indicating the polymerization behaviour of $^{c/t}$**DDDC**, ^{t}**DDDC**, and **TPDC** are illustrated in *Figure 2*, *Figure 3* and *Figure 4*, respectively. The following results revealed that the copper compounds listed above are effective catalysts for polymerization of three cyclic dimers regardless of the valence of copper and the counter anion.

Three copper compounds lowered the temperature at which polymerization of each cyclic dimer starts (hereafter denoted polymerization temperature) of $^{c/t}$**DDDC**, while no lowering effect was found when **DCP** was used (*Figure 2*). The fact that the Cu(acac)$_2$-containing sample had the lowest peak-top temperature suggests that Cu(acac)$_2$ has the most effect in lowering the polymerization temperature. It also should be noted that the temperature range in which an exothermic peak is observed for Cu(acac)$_2$-catalyzed

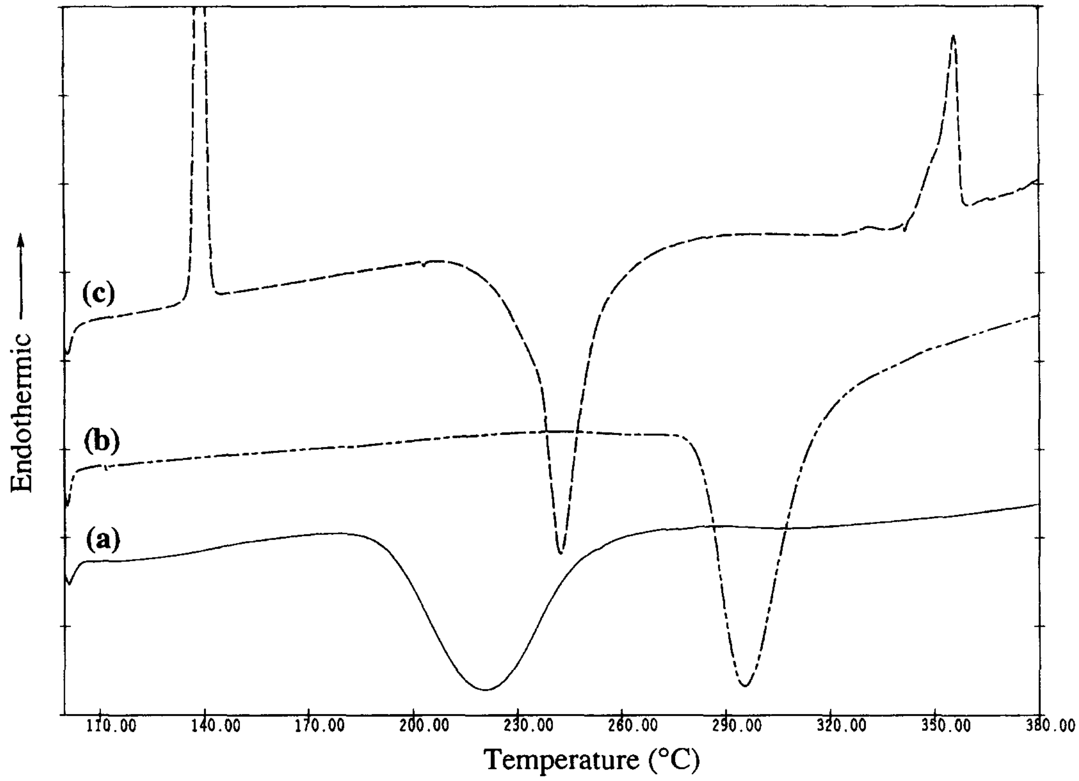

Figure 1 The d.s.c. heating thermograms of (a) $^{c/t}$**DDDC**, (b) ^{t}**DDDC**, and (c) **TPDC**

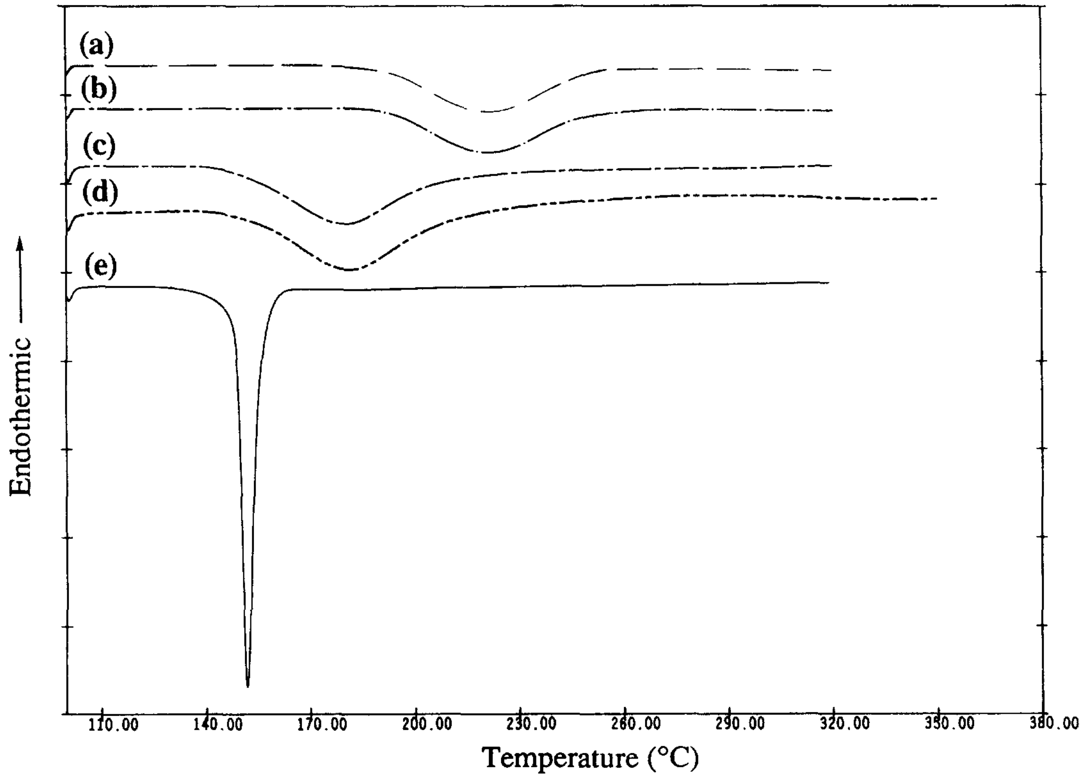

Figure 2 The d.s.c. heating thermograms of $^{c/t}$**DDDC** (a) without catalyst, (b) with **DCP**, (c) with CuCl, (d) with CuCl$_2$, and (e) with Cu(acac)$_2$

polymerization is much sharper than those for runs using CuCl or $CuCl_2$. This suggests the greater rate of the $Cu(acac)_2$-catalyzed polymerization compared with the other two catalysts is due to the better miscibility of $Cu(acac)_2$ with $^{c/t}$**DDDC**.

A decrease in polymerization temperature by the addition of copper compounds was also observed in the case of ^{t}**DDDC** (*Figure 3*). Two exothermic peaks, including one very sharp peak, were detected when $Cu(acac)_2$ was used. The first exothermic peak, which is much sharper than that observed for $^{c/t}$**DDDC**, is attributable to polymerization of ^{t}**DDDC**, while the second peak may be attributed to polymerization of the remained ^{t}**DDDC**. The cyclic dimer would probably have remained due to quick solidification of

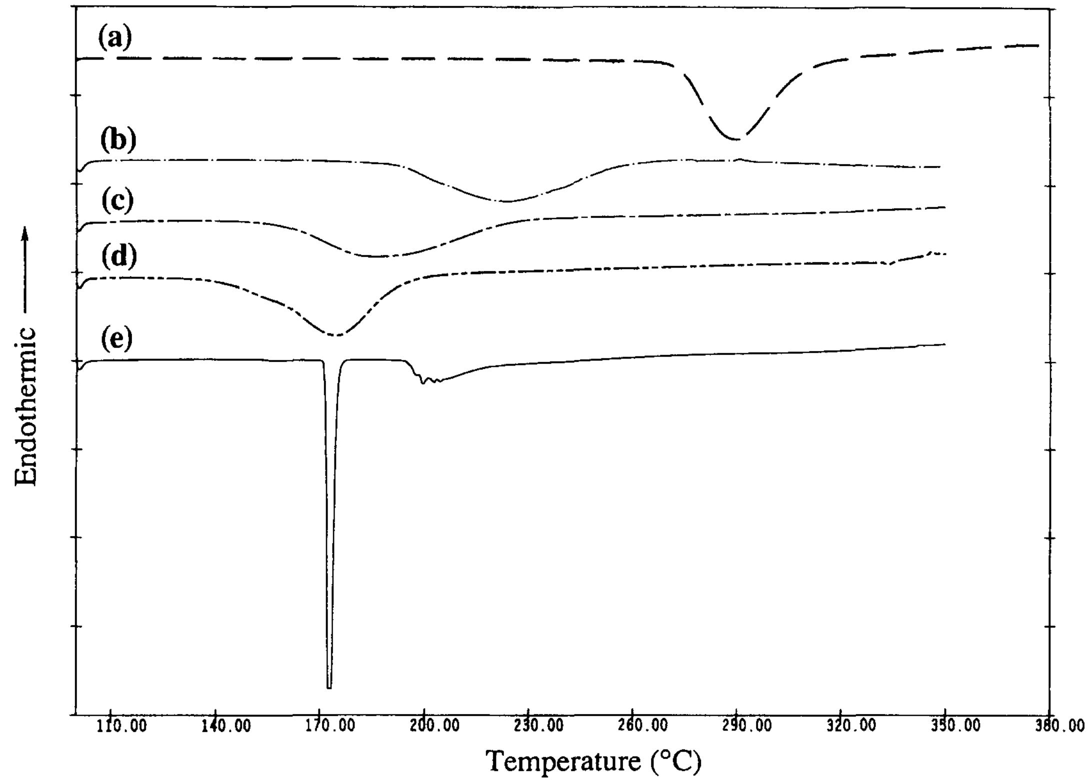

Figure 3 The d.s.c. heating thermograms of ^{t}**DDDC** (a) without catalyst, (b) with **DCP**, (c) with CuCl, (d) with $CuCl_2$, and (e) with $Cu(acac)_2$

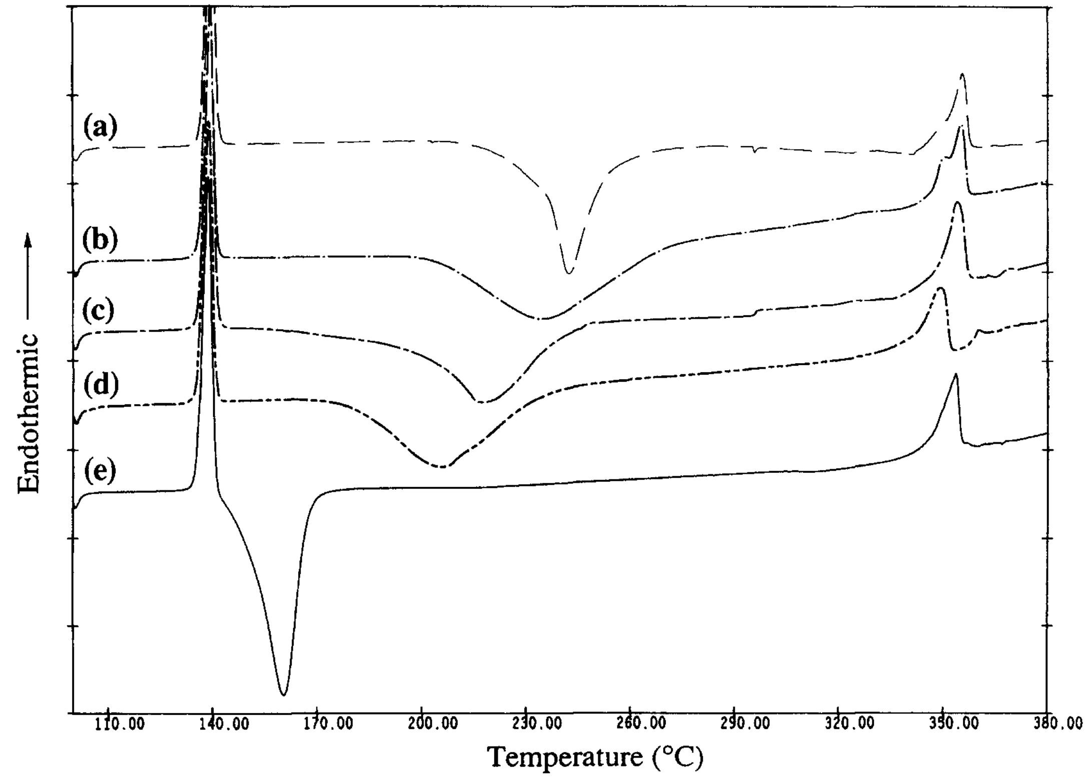

Figure 4 The d.s.c. heating thermograms of **TPDC** (a) without catalyst, (b) with **DCP**, (c) with CuCl, (d) with $CuCl_2$, and (e) with $Cu(acac)_2$

the reaction medium by very fast polymerization, as indicated by the extremely sharp peak described above. In other words, this dimer would polymerize in two steps at *ca.* 170 and 200°C to yield **PMPSM**. The sum of enthalpies of the two exothermic peaks is almost the same as that for $^{c/t}$**DDDC**, suggesting that these two peaks are ascribed to the polymerization of ^{t}**DDDC**. It is of great interest that the polymerization temperature was lowered in a **DCP**-containing formulation, suggesting that this radical initiator is effective for polymerization of ^{t}**DDDC**. This forms a striking contrast to the polymerization behaviour of $^{c/t}$**DDDC**. Since it is not reasonable to consider a significant difference in the thermal polymerization activity between cis and trans **DDDC** isomers, the result obtained above must be caused by some contaminants in $^{c/t}$**DDDC**.

Finally, the effects of copper compounds on polymerization of **TPDC** were similar to those for $^{c/t}$**DDDC** and ^{t}**DDDC**, although the polymerization temperature in the presence of $Cu(acac)_2$ was a little lower than those for CuCl or $CuCl_2$-catalyzed polymerization (*Figure 4*). **DCP** slightly lowered the polymerization temperature of **TPDC**. This lowered polymerization temperature is in agreement with a catalytic effect of **DCP** reported previously[31].

It has already been reported that platinum and rhodium compounds inhibit the polymerization of **TPDC**[19] but are very active for polymerization of **DDDC**[21]. In fact, polymerization of **DDDC** did not take place by heating below 100°C with the copper catalysts examined, whereas **PMPSM** having high molecular weight was formed even at room temperature in the presence of platinum or rhodium catalysts.

Polymerization of DDDC using copper catalyst

The catalytic activity of three copper compounds, CuCl, $CuCl_2$, and $Cu(acac)_2$, toward polymerization of **DDDC** was examined in xylene at the reflux temperature. These three compounds were effective catalysts to synthesize **PMPSM** when $^{c/t}$**DDDC** was used as a starting material. $Cu(acac)_2$ did not initiate the polymerization of ^{t}**DDDC**, whereas **PMPSM** was obtained when CuCl or $CuCl_2$ was used as a catalyst. This can be explained by the polymerization temperature of ^{t}**DDDC** at around 170°C in the d.s.c. analysis (*Figure 3*), which is higher than the reaction temperature in xylene solution. As a matter of fact, the d.s.c. traces for formulations containing CuCl or $CuCl_2$ displayed very wide peaks with a polymerization temperature of around 140°C.

The dependence of the [dimer]/[catalyst] molar ratio on the M_n of the resulting **PMPSM** was investigated using CuCl. When the molar ratios were 2000, 1400 and 300, the M_n of **PMPSM** were 4.7×10^4, 1.3×10^4 and 3.9×10^3, indicating that the higher [dimer]/[catalyst] molar ratio gives the higher molecular weight of **PMPSM**. Although the linear relationship between these two parameters was not observed and the M_ns of polymers were significantly smaller than the calculated values based on the living polymerization mechanism, there can be a meaningful interaction between the catalyst and polymer chains to alter the molecular weight of **PMPSM**.

Polymerization of DDDC in the presence of trimethylchlorosilane

$^{c/t}$**DDDC** polymerizes at temperatures lower than those for polymerization of ^{t}**DDDC** as described above. Because a small amount of chlorosilanes or hydroxysilanes, which can be a possible initiator for the polymerization of $^{c/t}$**DDDC**, is suspected as described in the Experimental section, the polymerization behaviour of ^{t}**DDDC** in the presence of trimethylchlorosilane (**TMSCl**) or trimethylhydroxysilane (**TMSOH**) was examined by d.s.c. analysis and a sealed-tube experiment.

Table 1 Polymerization of ^{t}**DDDC** using **TMSCl** or toluene

Run	Additive (amount[a])	Yield (%)[b]	M_w (g.p.c)	M_w/M_n
1	None	75	2 640 000	4.1
2	**TMSCl** (0.08)	79	648 000	4.1
3	**TMSCl** (0.37)	81	269 000	2.4
4	**TMSCl** (3.90)	55	90 000	2.0
5	Toluene (4.80)	32	1 950 000	4.4
6	Toluene (19.4)	7	740 000	4.3

[a] [Additive]/[^{t}**DDDC**] molar ratio
[b] Isolated yield

The polymerization temperature of ^{t}**DDDC** was lowered from *ca.* 270°C to *ca.* 210°C when a small amount of **TMSCl** was present, whereas no lowering effect on the polymerization temperature was found when **TMSOH** was used. This suggests that **TMSCl** participates in an initiation step of ring-opening polymerization. Hence, the cause of lower polymerization temperature of $^{c/t}$**DDDC** in comparison with ^{t}**DDDC** is deduced to be the residual chlorosilane(s), $ClCH_2MePhSiCl$ and/or $ClCH_2MePhSiCH_2MePhSiCl$, although these compounds have not been identified due to their low concentration in $^{c/t}$**DDDC**.

An effect of **TMSCl** toward polymerization of ^{t}**DDDC** was also examined by a sealed-tube experiment. The results are summarized in *Table 1* along with data of two runs using toluene† as an additive. In all runs except for Run 4, the polymerization product was a homogeneous mixture, whereas a heterogeneous mixture (a polymer phase and a **TMSCl** phase) was observed in Run 4. It can be observed that increasing the amount of **TMSCl** lowers the molecular weight (M_w) of the resulting **PMPSM**. In addition, M_w of **PMPSM** produced in the presence of **TMSCl** (Run 4) is significantly lower than **PMPSM** obtained using a similar amount of toluene (Run 5). M_ws of **PMPSM** samples in Runs 4 and 5 must be close to each other if **TMSCl** works as a diluent as toluene does. These results, therefore, also suggest participation of **TMSCl** in the polymerization of ^{t}**DDDC**. While the polymerization mechanism has not been fully investigated, hydrochloric acid formed by the hydrolysis of chlorosilane(s) with a trace amount of water in the reaction medium might be responsible for the catalytic effect of **TMSCl**. In fact, the resonance assignable to the terminal Me_3SiC group should be recorded in the ^{29}Si n.m.r. spectrum of **PMPSM** if **TMSCl** is an active species, but no resonance assignable to the terminal group was observed for **PMPSM** formed by this method.

Copolymerization of DDDC and TPDC

Copolymerization of ^{t}**DDDC** and **TPDC** was studied by a non-catalytic bulk method. The characteristics of the products are listed in *Table 2*. Six copolymers with various $MePhSiCH_2$ (**MP**)/Ph_2SiCH_2 (**DP**) unit ratios were obtained in high yield. Solubility of **PDPSM** has improved appreciably by incorporation of an **MP** unit into the polymer backbone. A copolymer containing **MP** units greater than 27 mol% is not insoluble, but swells in THF. The THF-insoluble fraction decreased with an increasing content of

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† Toluene was used due to its good miscibility with ^{t}**DDDC** and relatively low boiling temperature.

Table 2 Synthetic results of copolymerization

Sample ID	**DDDC/ TPDC** molar ratio[a]	Conversion (%)	THF-insoluble fraction (wt. %)	M_w (g.p.c.)[c]
1	0/100	99	> 99	–
2	27/73	99	91[b]	335 000
3	49/51	97	55[b]	894 000
4	69/31	99	12[b]	1 130 000
5	85/15	98	0	1 110 000
6	100/0	99	0	2 020 000

[a] Loaded molar ratio
[b] Swollen in THF
[c] THF-soluble component

Table 3 Unit ratios in copolymers estimated by ^{29}Si n.m.r. analysis

Sample ID	Analytic condition	**MP/DP** unit ratio	Note
2	Solid state	28/72	As-prepared
2-I	Solid state	27/73	THF-swollen part
3	Solid state	51.5/48.5	As-prepared
3-S	$CDCl_3$ solution	56/44	THF-soluble part
3-I	Solid state	47/53	THF-swollen part
4	Solid state	70/30	As-prepared
4-S	$CDCl_3$ solution	70/30	THF-soluble part
4-I	Solid state	60/40	THF-swollen part
5	$CDCl_3$ solution	85/15	As-prepared

MP unit in copolymers and the copolymers became completely soluble when the **MP** content was greater than 85 mol%. These results suggest that the high crystallinity observed in **PDPSM** is hampered by the formation of copolymers.

Copper-catalyzed copolymerization of ^{t}**DDDC** and **TPDC** was also examined in xylene solution. A copolymer with the **MP/DP** unit ratio of 72/28 being close to the load ^{t}**DDDC/TPDC** ratio of 69/31 was obtained when CuCl was used as a catalyst. The conversion of dimers to a copolymer was slightly lower than that for the non-catalytic polymerization. Copolymerization using $Cu(acac)_2$ also successfully proceeded to yield a copolymer with the **MP/DP** unit ratio of 79/21 while the loaded ratio was 69/31. The difference between the two values is ascribed to the very low conversion, *ca.* 20%, of dimers to a copolymer as will be discussed in the 'Dimer reactivity ratio' section.

N.m.r. studies of the copolymers

Copolymers 2–4 in *Table 2* were fractionated by the solubility difference in THF, and the **MP/DP** unit ratios of, in total, nine samples including four as-prepared samples, were estimated by ^{29}Si n.m.r. spectrometry. The results are listed in *Table 3*. The **MP/DP** unit ratios of four as-prepared samples are in fair agreement with those of the loaded ^{t}**DDDC/TPDC** ratio, suggesting that copolymers with the desirable **MP/DP** unit ratios can be prepared by the non-catalytic method. One can easily see the differences between the **MP/DP** values of several pairs of samples obtained by fractionation. As expected, each THF-soluble part of copolymers has higher **MP** contents than the corresponding THF-swollen part. According to these results, copolymers with **MP** contents as high as 70 mol% seem soluble in organic solvents such as THF.

It is also notable that each THF-soluble copolymer exhibited a very sharp resonance at −4.8 ppm, which can be assigned to silicon of **MP** units. Three resonances assignable to **DP** units are observed at −8.7, −9.0, and −9.4 ppm. The ^{29}Si n.m.r. spectrum of 4-S is shown in *Figure 5*. The presence of these three resonances suggests that the chemical shift of the silicon atom in **DP** units is affected by the remote units as well as the adjacent units. On the other hand, the presence of only one sharp resonance indicates that the neighbouring chemical environment does not affect the chemical shifts of silicons in **MP** units.

Four resonances attributable to four types of sequential orders of MMDDMM, MMDDDD, MMDDDD, and DDDDDD where M and D denote **MP** and **DP**, respectively, are possible in the **DP** unit region if one considers six sequential units (three dimeric units). Since only three resonances were observed in the spectrum, two in the possible four resonances probably merged into one. The relative intensity of the peak at − 8.7 ppm increased with increasing the **MP/DP** unit ratios of copolymers, and that of the peak at −9.4 ppm increased with decreasing the **MP/DP** unit ratios. These results indicate that the resonances at −8.7 and −9.4 ppm can be assigned to silicons in the MMDDMM and DDDDDD sequences, respectively. One or both of silicons in the MMDDDD and MMDDDD sequences are responsible for the centre resonance at −9.0 ppm.

The ^{13}C n.m.r. analysis of THF-soluble components was also informative to study the sequential order of the present copolymers. A resonance at around 2.1 ppm is assignable to the methylene carbon of $MePhSiCH_2Ph_2Si$ units because this resonance is not observed for **PMPSM** homopolymer. The $[MePhSiCH_2Ph_2Si]/\{[MePhSiCH_2MePhSi] + [Ph_2SiCH_2Ph_2Si]\}$ unit ratio of 3-S calculated by the ^{13}C n.m.r. spectrum is 26/74, whereas that of an ideal random copolymer with the same **MP/DP** unit ratio is 25/75. This suggests that both **MP** and **DP** units are almost randomly distributed in the copolymer. A copolymer with the **MP/DP** unit ratio of 28/72 obtained by CuCl-catalyzed polymerization exhibited the distribution of **MP** and **DP** units being similar to that of sample prepared by non-catalytic polymerization. Hence, the copolymer obtained by the Cu-catalyzed method also seems to be a random copolymer.

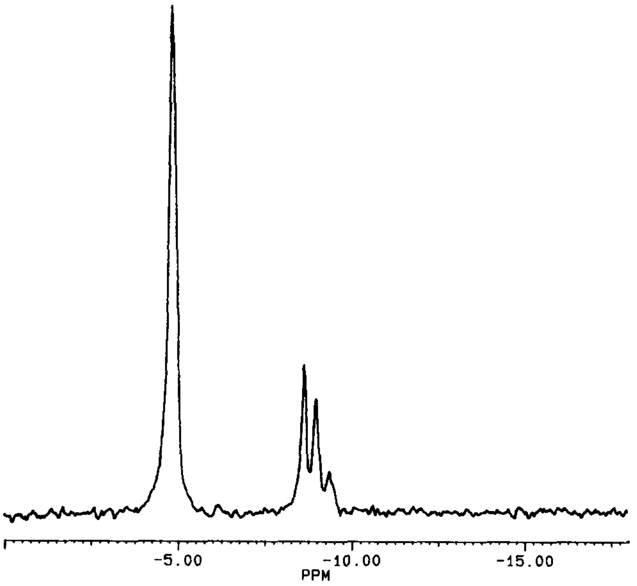

Figure 5 The ^{29}Si n.m.r. spectrum of 4-S

Dimer reactivity ratio on copolymerization of **DDDC** *and* **TPDC**

The monomer reactivity ratio, denoted the dimer reactivity ratio in this article because cyclic dimers were used as starting materials, was examined by bulk copolymerization without catalyst. The reaction was carried out in a sealed tube at 300°C under the condition at which the conversion of dimers to a copolymer was below 10%. The relationship between ^{t}**DDDC** contents in dimer mixtures and the **MP** contents in copolymers is illustrated in *Figure 6* where the solid line represents the observed relationship and the broken line represents a relation for the ideal copolymerization. It is evident that the **MP** contents in copolymers are slightly higher than the values for the ideal copolymerization regardless of the ^{t}**DDDC** contents. These results suggest that ^{t}**DDDC** tends to be easily incorporated into copolymers compared with **TPDC** in the initial stage of copolymerization.

The reactivity ratios, r_1 and r_2 for copolymerization of ^{t}**DDDC** (dimer-1) and **TPDC** (dimer-2), were estimated by the Finemann–Ross method[34]

$$F - F/f = r_1 \times F^2/f - r_2$$

The parameter $F - F/f$ as a function of F^2/f is shown in *Figure 7* where F is the [^{t}**DDDC**]/[**TPDC**] molar ratio in each dimer mixture, and f is the **MP/DP** unit ratio of each copolymer. The values r_1 and r_2 estimated by the above equation are 1.56 ± 0.1 and 0.56 ± 0.04, respectively. This non-catalytic copolymerization is found to be almost random copolymerization because both r_1 and r_2 are relatively close to unity. Both values are exactly equal to unity for the ideal completely random copolymerization. This set of r_1 and r_2 reflects the fact that the **MP/DP** unit ratios of resulting copolymers are slightly higher than the corresponding [^{t}**DDDC**]/[**TPDC**] molar ratio in the dimer mixtures.

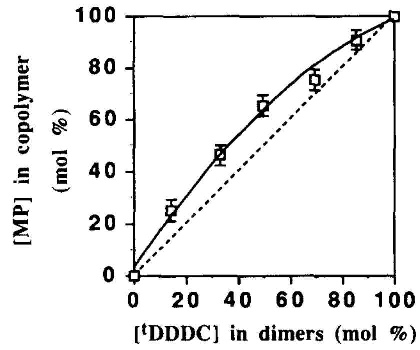

Figure 6 The relationship between ^{t}**DDDC** contents in dimer mixtures before copolymerization and the **MP** contents in the resulting copolymers

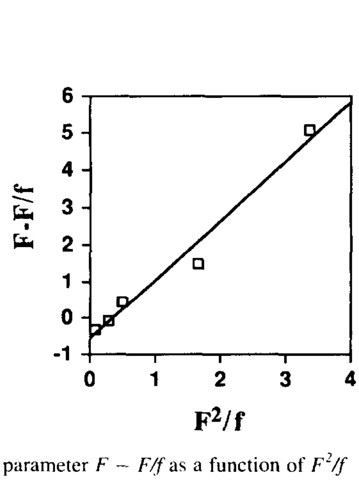

Figure 7 The parameter $F - F/f$ as a function of F^2/f

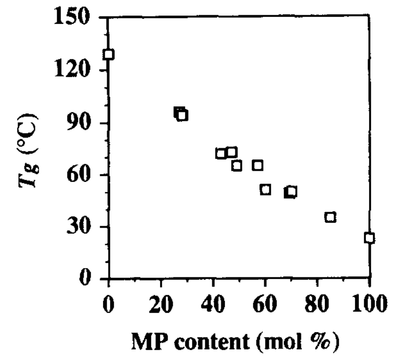

Figure 8 T_g values as a function of **MP** content

Thermal properties of the copolymers

A d.s.c. study was conducted to identify the transition temperatures of copolymers prepared by the non-catalytic method. The glass transition temperatures (T_gs) of ten samples ranged from 35 to 96°C, while those of two homopolymers, **PMPSM** and **PDPSM**, were 23 and 130°C, respectively. The T_gs as a function of **MP** contents are illustrated in *Figure 8*. The T_gs decrease monotonously with increasing **MP** contents of the copolymers. Because no sign of the glass transition at around 23°C was detected, it is evident that each copolymerization product is not a mixture that contains a **PMPSM** homopolymer but a homogeneous copolymer.

The melting–crystallization behaviour of these copolymers is also of great interest from the point of view of processability. According to the d.s.c. analysis, copolymers with **MP** contents below 50 mol% exhibited the melting temperatures (T_ms). In other words, these copolymers were found to be crystalline polymers. The shapes of both melting and crystallization peaks of these copolymers were quite similar to those of **PDPSM** homopolymer. In addition, the T_ms and the heats of fusion (ΔH_ms) also decreased monotonously with increasing **MP** content. Hence, the degree of crystallinity of these copolymers decreased as the **MP** content increased.

The thermal transition behaviour of six samples including four copolymers with various **MP/DP** unit ratios and two homopolymers was also examined by dynamic mechanical analysis. The temperature dependences of the storage modulus and tan δ are illustrated in *Figure 9(A)* and *Figure 9(B)*, respectively. In *Figure 9(B)*, a distinct peak of the tan δ at the T_g was observed for each sample. The intensities of these peaks decrease with decreasing **MP** contents of samples, suggesting that the motion of polymer chains at T_gs decreased as the **MP** content decreased. The degree of sharpness of these peaks showed a similar tendency, implying a decrease of the sharpness with decreasing **MP** content. This peak pattern also reflects the motion of polymer chains at the T_gs. The storage moduli of three completely amorphous copolymers (samples 4, 5, and 6 in *Table 3*.) dropped steeply to below 10^7 dyn/cm^2 as depicted in *Figure 9(A)*. This is characteristic behaviour for a unidimensional amorphous polymer. It is notable that the storage modulus of 2 dropped from *ca.* 10^{10} dyn/cm^2 at room temperature to 10^8 dyn/cm^2 at 250°C while that of a polymer blend comprising **PDPSM** and **PMPSM** with an

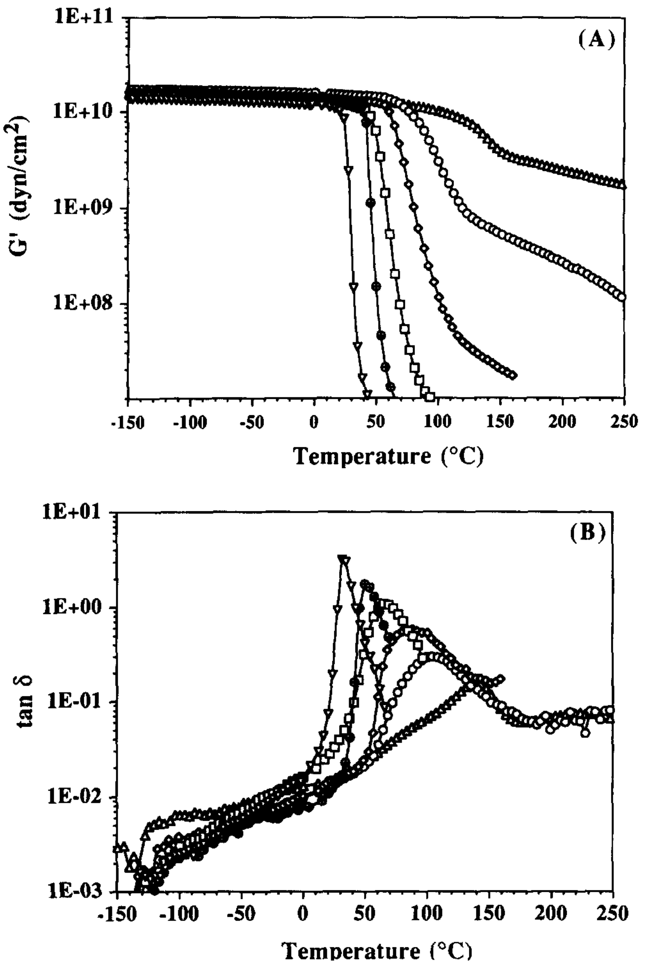

Figure 9 The temperature dependence of (A) the storage moduli and (B) tan δ for four copolymers and two homopolymers. 1 (△), 2 (○), 3 (◇), 4 (□), 5 (⊕), and 6 (▽)

MP content of 27 mol% still remained at 10^9 dyn/cm^2 at 250°C. This is caused by the lower crystallinity in the copolymer compared with **PDPSM**.

Block copolymerization of DDDC and TPDC

The copolymers described in the above sections are almost random copolymers although some deviations of the distributions of two dimeric units from the ideal distribution were observed. Synthesis of **PMPSM-PDPSM** block copolymers is of great interest because **PMPSM/PDPSM** blends containing **PDPSM-PMPSM** block copolymers presumably formed during preparation of the polymer blends displayed more finely-dispersed texture than blends without the block copolymers[30,31].

First, bulk polymerization without catalyst was attempted by employing a sequential addition method in which **TPDC** is added after the conversion of **DDDC** to **PMPSM** is completed. The ^{29}Si n.m.r. analysis showed the **MP/DP** unit ratio of the product to be almost identical to the loaded **DDDC/TPDC** ratio. Solvent extraction is a useful method to characterize the product because a **PDPSM** homopolymer is insoluble in common solvents while **PMPSM** shows good solubility. The ^{29}Si n.m.r. analysis indicated that the THF-soluble product was **PMPSM** and the insoluble part was **PDPSM**, suggesting that formation of **PMPSM-PDPSM** block copolymers did not take place, probably due to the poor compatibility of **TPDC** with **PMPSM**.

The catalytic polymerization using copper catalysts was also examined as an alternative method. Pt and Rh compounds are not applicable because they act as inhibitors for **TPDC** polymerization[19]. Only the formation of **PDPSM** and **PMPSM** homopolymers was achieved regardless of the kinds of copper compounds. It was hence demonstrated that catalytic polymerization of **TPDC** did not initiate at the reactive **PMPSM** terminal sites to yield **PMPSM-PDPSM** block copolymers, although **PMPSM** and **TPDC** were both homogeneously dissolved in xylene. There seem to be some interactions between propagating **PMPSM** polymer chains and a copper catalyst, as demonstrated by the relationship between the [dimer]/[catalyst] molar ratio and the molecular weight of the resulting **PMPSM**, but insufficient to control the structure of polymers such as the molecular weight and the terminal group. Development of a modified polymerization system including co-catalysts is necessary to overcome this problem.

CONCLUSIONS

Catalytic and non-catalytic ring-opening polymerization behaviour of two phenyl-substituted 1,3-disilacyclobutanes were investigated. Three copper compounds showed catalytic activities toward synthesis of poly(methylphenylsilylenemethylene) (**PMPSM**) from 1,3-dimethyl-1,3-diphenyl-1,3-disilacyclobutane (**DDDC**) although they were not as active as Pt or Rh compounds. The dependence of the molecular weight of **PMPSM** on the [dimer]/[catalyst] molar ratio was observed, indicating some interactions between **PMPSM** chains and copper catalyst. However, block copolymerization of **DDDC** and 1,1,3,3-tetraphenyl-1,3-disilacyclobutane (**TPDC**) was not successful. Copolymerization of **DDDC** and **TPDC** with or without catalyst yielded copolymers with [MePhSiCH$_2$]/[Ph$_2$SiCH$_2$] ratios very close to the loaded [**DDDC**]/[**TPDC**] ratios. The results of n.m.r. analysis and the dimer reactivity ratio suggest that the resulting copolymers are almost random copolymers. The dimer sequential length distributions, however, are slightly different from an ideal random distribution of the two dimeric units.

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