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Synthesis and thermal properties of diphenylsiloxane block copolymers

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Abstract

Three series of polydiphenylsiloxane (PDPS)-containing diblock copolymers were synthesized with controlled molecular weight and composition by sequential addition of the corresponding comonomers through a living anionic polymerization. These copolymers included poly(diphenylsiloxane-b-dimethylsiloxane) (PDPS/PDMS), poly(diphenylsiloxane-b-methylphenylsiloxane) (PDPS/PMPS), and poly(diphenylsiloxane-b-methyltrifluoropropylsiloxane) (PDPS/PMFPS). The structural effect of the soft segment of these PDPS-containing diblock coploymers on the mesophase transition behaviors was examined. The observations with differential scanning calorimetry (DSC) and polarized optical microscopy (POM) were combined to determine the actual thermal transition behaviors. Critical compositions for the appearance of these thermal transitions were determined for each series of the diblock copolymers. The thermal transition properties, such as temperature and peak shape were also correlated to the structures of the copolymers. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Diphenylsiloxane block copolymer; Mesophase; Thermal transition

1. Introduction

Poly(diphenylsiloxane) (PDPS) is a highly crystalline polymer with a crystal-to-mesophase-state transition temperature (T_m) over 250°C, and a mesophase-to-isotropic-state transition temperature (T_i) above 500°C [1–4]. In our previous paper [5], the flexible end-group on PDPS was found to decrease the T_m and T_i of PDPS. Moreover, the critical molecular weight based on molecular weight (M_n) for mesophase formation was also found to increase with an increase in the chain length of the flexible end-group. A sufficient long flexible end-group may lead to lower the T_m and T_i of PDPS. So that the PDPS can become easily characterized and injection-molding applicable.

As early as in 1969, Bostick [6] had reported the synthesis and ^{1}H NMR characterization of Poly(diphenylsiloxane-b-dimethylsiloxane) (PDPS/PDMS) diblock copolymer. However, the melting behavior of the crystal-liquid crystal transition for PDPS/PDMS block copolymers was first suggested by Meier et al. [7] in 1985. We have studied the behavior of such transition for a series of PDPS/PDMS diblock copolymers with the M_n values around 40k ($k = 1000$) and the PDPS content less than 50 mol% [8]. For these copolymers, the phase transition temperatures (defined as T_c in that paper) were found to have a linear relationship with the molar percentage of PDPS.

Recently, the mesophase of PDPS was suggested to be a condis-crystal rather than just a liquid crystal [9]. Therefore, T_m was used to replace T_c for the crystal to mesophase transition temperature in this paper.

In addition to PDPS/PDMS, we are also interested in PDPS/PMPS (polymethylphenylsiloxane) and PDPS/PMFPS [poly-methyl(3,3,3-trifluoropropyl)siloxane] diblock copolymers with wild range of Ph_2SiO contents and M_n. The thermal properties of these types of copolymers were still unknown. The goal of this study is to synthesize and characterize these PDPS-containing diblock copolymers. Emphasis is put on correlating the flexible segments to the thermal transition behaviors in order to understand more about the mesophase behavior of the PDPS moiety in the copolymers.

2. Experimental

2.1. Materials

Hexamethylcyclotrisiloxane (D_3) (Dow Corning),

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hexaphenylcyclotrisiloxane (P_3) (Dow Corning), methyl (3,3,3-trifluoropropyl)cyclotrisiloxane (F_3) (Dow Corning), diphenylmethylchlorosilane (Hüls), and *n*-butyllithium (Merck) were used as purchased without further purification. Trimethyltriphenylcyclotrisiloxane (D_3^{ph}) was obtained as a distillate from the pyrolysis product of a crude mixture of methylphenylsiloxane cyclic oligomers (Dow Corning) in the presence of lithium hydroxide. Tetrahydrofuran (THF) and toluene, which were already refined according to regular methods, were freshly distilled into the reaction flask under purified and dried argon gas just before use.

2.2. Synthesis of the copolymers

Three series of PDPS-containing diblock copolymers, PDPS/PDMS, PDPS/PMPS, and PDPS/PMFPS, were synthesized by sequential polymerization. A living anionic polymerization of the corresponding trimer — D_3, D_3^{ph} or F_3 was followed by P_3. The following is a general procedure for the synthesis. The anionic living ring-opening polymerization was conducted in an anhydrous THF (for PDMS and PMPS) or toluene (for PMFPS) system under argon at the reflux temperature. A stoichiometric amount of *n*-BuLi/hexane solution was used as an initiator. After the addition of P_3, the reactor was heated to 160°C for 1–6 h depending on PDPS content. The products was dissolved in THF or diphenyl ether and terminated by $Ph_2MeSiCl$. The copolymer was obtained as precipitate from methanol. The product was filtered and dried with vacuum stripping at 60°C overnight.

The synthesized copolymers were characterized by ^{1}H NMR, ^{29}Si NMR and gel permeation chromatography (GPC). For few THF-insoluble solid PDPS/PDMS copolymers, for example: D_6P_{32}, $D_{323}P_{91}$, etc. the molecular weight was estimated based on the M_n of the first polymerized PDMS segment (determined by GPC) and the PDPS mol% of the final copolymers (determined by solid ^{29}Si NMR).

The thermal transition temperatures (T_g, T_m, and T_i) and the thermal stability of all the copolymers were studied with POM, DSC, and TG techniques. The glass transition temperature and mesophase transition temperature were recorded on DSC after the following thermal treatments on the copolymers. The copolymers were first heated to 300°C in order to eliminate any previous thermal history, then cooled to 50°C for 10 min at a rate of 10°C min^{-1} and subsequently re-heated at the same rate. The T_m, which measured by DSC was checked again by POM observation. The isotropization temperature (T_i) or the so-called clearing temperature was determined by POM at the temperature of disappearance of birefringence.

2.3. Measurement

^{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.

Molecular weights were obtained by GPC (Kratos Model Spectroflow 400) using THF or toluene as the eluent with Shodex KF-804, KF-803, KF-802, KF-801 columns. The reported molecular weights and molecular weight distributions were calculated on the basis of the retention volumes of the polymers relative to those of the polystyrene standards. DSC scans were measured on a DuPont 9900 thermal analyzer at a heating rate of 10°C min^{-1}. POM was performed on an Olympus BX50 polarizing microscope equipped with a Linkam TMS92 hot stage.

3. Results and discussion

3.1. PDPS/PDMS diblock copolymer

In 1990, Ibemesi et al. prepared PDPS/PDMS block copolymers by polymerizing the diphenylsiloxane block first and then followed by polymerization of the dimethylsiloxane block [10]. In this study, we used THF instead of diphenyl ether as polymerization solvent to prepare PDMS/PDPS block copolymers by polymerizing the dimethylsiloxane block first [11]. The copolymers with M_n ranges from 1.5 to 70k and PDPS content ranges from 5 to 90 mol% ($DP_{PDPS} = 7–200$) were synthesized and characterized. We have reported the T_gs of the PDPS/PDMS diblock copolymers [8] with M_n around 40k and PDPS content <50 mol%. There, the copolymer has a T_g around that of the PDMS homopolymer and no significant change was observed. However, for the relatively small polymer molecules prepared in the present study (for example, $M_n \cong 13k$), the T_g was disappearing when PDPS content ≥27 mol% or $DP_{PDPS} \geq 32$. We suggest that the length of the PDMS block in this copolymer is too short to behave the glass transition. In addition to the polymers reported in the previous work, the copolymers of high PDPS contents will be emphasized. We would like to focus on the T_m and T_i behavior of these block copolymers.

Fig. 1 is the typical DSC traces of the mesophase transition in DSC thermograms of PDPS/PDMS diblock copolymers. We have found that the DP of PDPS segment, rather than the PDPS mol% of the copolymer, affects the mesophase transitional peak shape more markedly. For example, the sample with 32.8 mol% of PDPS has a single sharp peak of T_m, but the sample with 77.8 mol% possesses dual peaks.

3.2. Critical compositions for the appearance of T_m and T_i

The temperatures of transforming crystalline phase to mesophase (T_ms) for these diblock copolymers were in the range of 120–260°C. The mesomorphic phase is similar to what was found in PDPS homopolymer [5]. The critical composition of PDPS/PDMS for the appearance of crystallinity as well as mesomorphic phase was observed. A

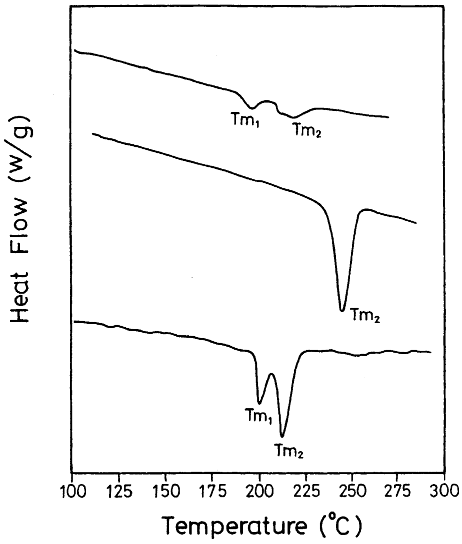

Fig. 1. DSC thermograms of PDMS/PDPS diblock copolymers (D = Me_2SiO, P = Ph_2SiO).

critical ratio of PDPS/PDMS for the appearance of crystallinity has been evaluated as shown in Fig. 2. A great change on the slope of this critical line happens in the range of $DP_{PDPS} = 15–25$ and goes steady after $DP_{PDPS} \geq 30$. The behavior of T_m is also greatly affected by the composition of the copolymers. T_m splits into T_{m1} and T_{m2} for the copolymer with a critical composition as shown in Fig. 3. In Fig. 3, copolymers without T_{mi} means that those samples transform from crystalline phase into the isotropic state directly after crossing the melting temperature. On the other hand, polymers with T_{m2} only (almost ≥200°C, with a composition of $DP_{DMPS} > 6$ and $DP_{PDPS} > 32$) is always decomposed before the complete transformation into the isotropic state, so we cannot observe their T_i from POM.

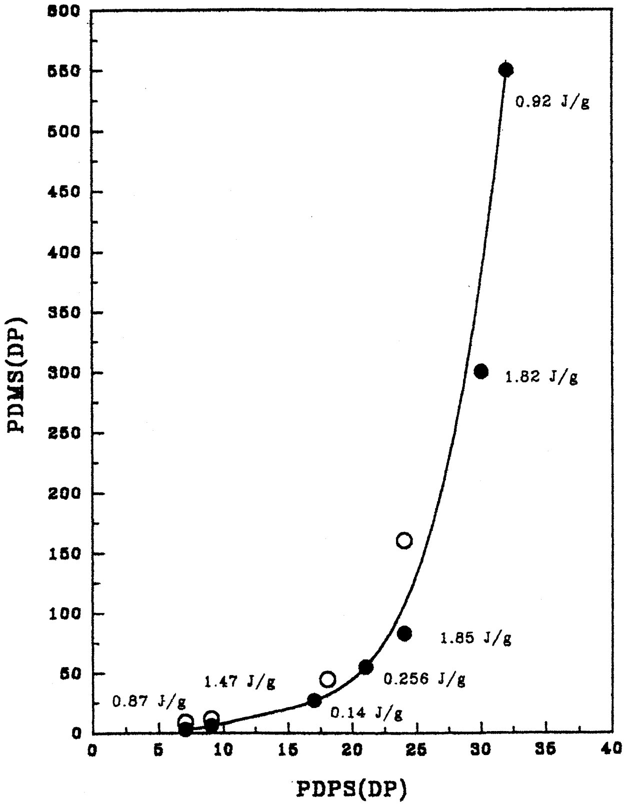

Fig. 2. The critical DP (degree of polymerization) of PDMS with definite DP of PDPS for the appearance of crystallinity of PDMS/PDPS diblock copolymers (● with T_m or T_i; ○ without T_m or T_i).

3.3. POM observation

Phase transitions of these copolymers were also observed with POM. The thermal treatments on the hot-stage are totally parallel to what performed on the DSC under same 10°C min^{-1} heating and cooling rates. Upon cooling these copolymers from isotropic state, similar spherulites with PDPS oligomers [5] were observed. No mesophase was observed for those oligo-copolymers with the DP of PDPS segment less than 12. Thus, their T_ms can also be assigned as T_is. On the other hand, for the copolymers with DP_{PDPS} larger than 12, the birefringence of mesophase gradually appeared upon cooling the crystalline copolymers from the melt. Subsequently, as cooling to the temperature below T_m from the mesophase, it results in spherulite textures. However, no distinguishable changes can be observed for T_{m1} and T_{m2}.

For the transition from the mesophase to the isotropic melt, no significant peak can be observed from DSC. These copolymers can be expected to undergo isotropization over a rather broad temperature range [5–9]. This purpose has been confirmed by POM, which shows a gradual reduction in the degree of birefringence as the sample is heated crossing the mesomorphic region and entering the isotropic state. The other copolymers with higher T_m become decomposed before melting into isotropic state. The critical composition for the appearance of T_i for the diblock copolymers is shown in Fig. 4.

The T_i increases with increasing M_n as well as PDPS mol%, and decreases with increasing PDMS mol%. It can

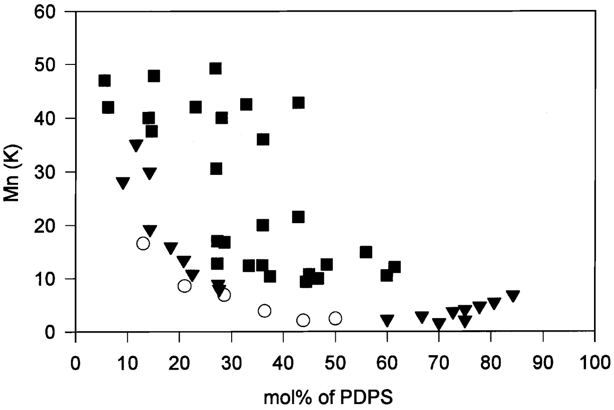

Fig. 3. The critical compositions of PDPS/PDMS diblock copolymers for the appearance of T_{mi} (▼ with T_{m1}/T_{m2}; ■ with T_{m2} only; ○ without T_{mi}).

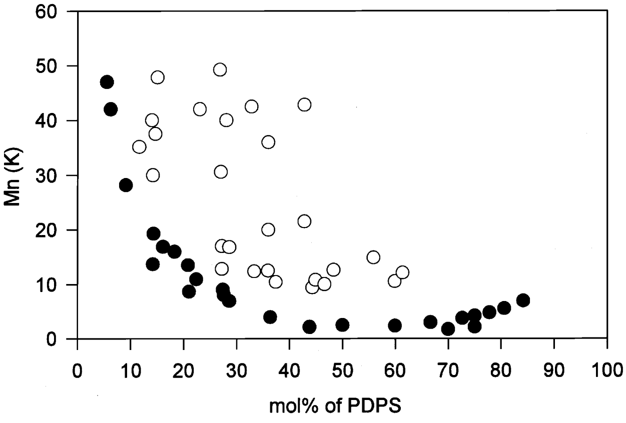

Fig. 4. The critical compositions of PDPS/PDMS diblock copolymers for the appearance of T_i (● with T_i; ○ without T_i).

reach up to 434°C without the decomposition of the copolymer. A compromise between DP_{PDPS} and DP_{PDMS} would lead to a high T_i, such as $D_{180}P_{32}$(T_i = 408°C) and $D_{107}P_{28}$(T_i = 434°C). Although, $D_{178}P_{28}$ has a greater M_n than $D_{107}P_{28}$ does, its T_i cannot be observed because of the decomposition.

3.4. Composition dependency for T_m

A pretty good relationship between T_{m2} and the composition of the copolymers was found. An approximately isothermal relationship of T_{m2} versus composition can be obtained for the PDPS/PDMS diblock copolymers as shown in Fig. 5. The origin of the multiple endotherm observed on this copolymer system will be discussed elsewhere.

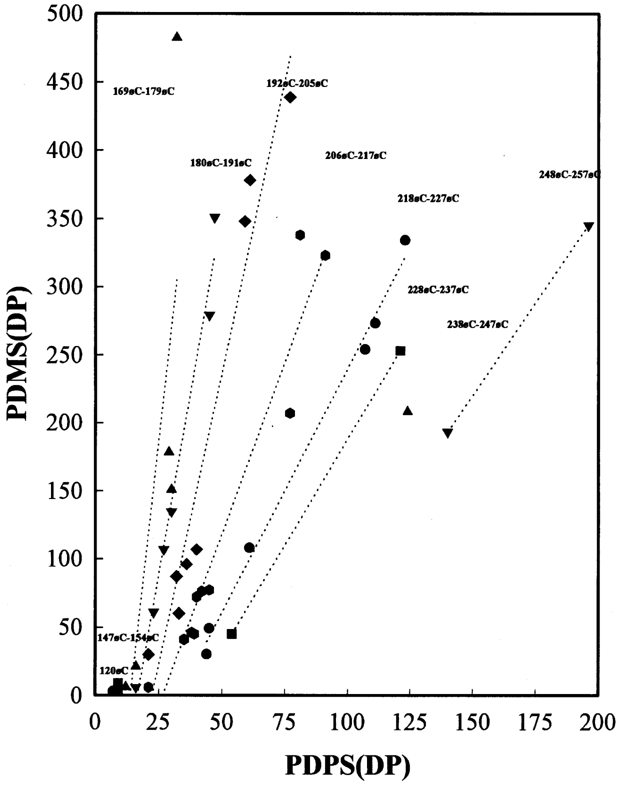

Fig. 5. Compositions of PDPS/PDMS diblock copolymers with constant T_{m2}.

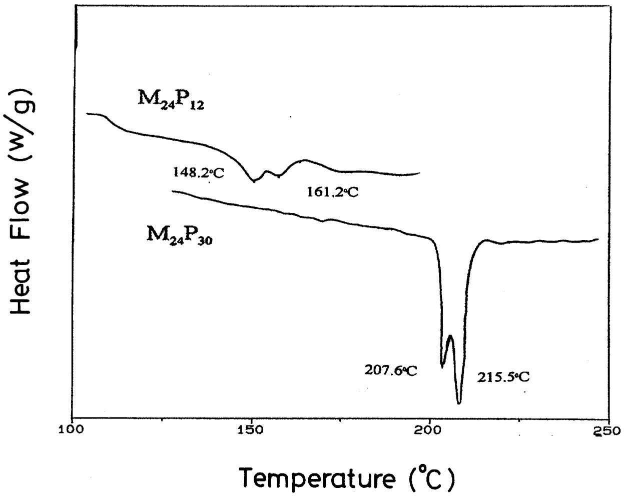

Fig. 6. DSC thermograms of $M_{24}P_{12}$ and $M_{24}P_{30}$ (M = MePhSiO ; P = Ph_2SiO).

3.5. PDPS/PMPS diblock copolymer

In order to compare the results of the PDPS/PMPS copolymers with that of PDPS/PDMS copolymers more effectively, only essential and comparable compositions of the copolymer are considered. By using the similar synthetic process, a series of PDPS/PMPS diblock copolymers with

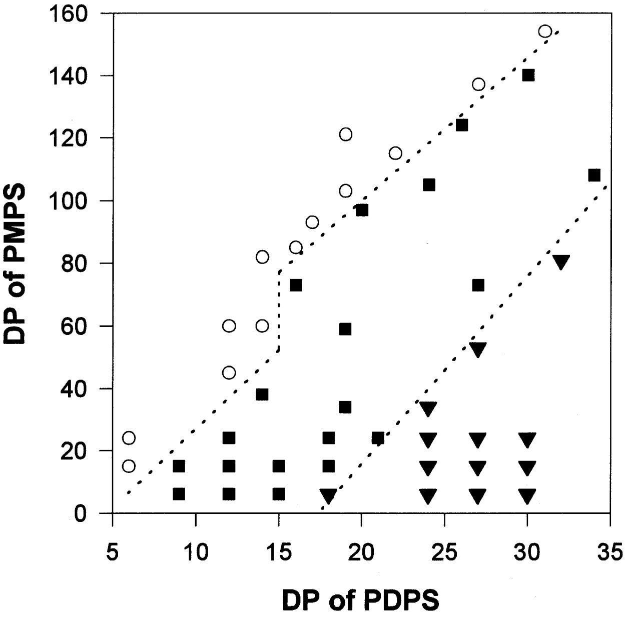

Fig. 7. The critical compositions of PDPS/PMPS diblock copolymers for the appearance of T_{mi} (▼ with T_{m1}/T_{m2}; ■ with T_{m1}, T_{m2} = T_i; ○ without T_{mi}).

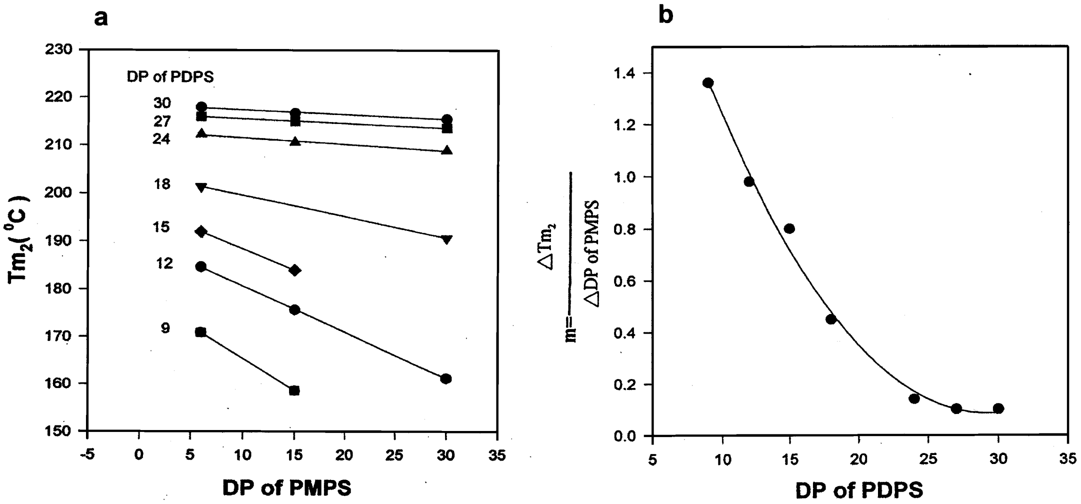

Fig. 8. T_{m2} as a function of DP of PMPS at constant DP of PDPS in PMPS/PDPS diblock copolymers.

narrow distributed molecular weight ($M_w/M_n \leq 1.36$), $M_n \leq 27.1$k and PDPS ≤ 82.3 mol% was synthesized and characterized. The T_gs and T_ms of these copolymers were determined by DSC. The T_gs were observed through whole range of PMPS contents in the temperature range around −16 to 24°C and that was close to the T_g of PMPS homopolymer (−20°C). However, it disappeared for the M_6P_n series when $DP_{PDPS} \geq 18$.

Fig. 6 is the typical thermograms of the PDPS/PMPS diblock copolymers. There are two peaks, assigned as T_{m1} and T_{m2}. Fig. 7 shows the critical composition of these series of copolymers for the appearance of T_m. With the help of POM, the T_{m2}s of many copolymers (in the middle band of Fig. 7) were found almost equal to the T_is. The mesophase behavior of these copolymers is ambiguous. Stable mesophase with both T_{m1} and T_{m2} was only found for the copolymers with $DP_{PDPhS} \geq 15$. An asymmetric substitution of the PMPS block leads to disturbance in crystallization of the PDPS block more than that done by PDMS. A sufficient length of PDPS chain is needed to resist the disturbance from PMPS chain. The mesophase transition behavior is not correlated well with the mol%. For example, $M_{45}P_{12}$ with a PDPS mol% of 21.5% does not provide T_m, whereas $M_{73}P_{16}$ with only a PDPS mol% of 14% provides a T_m.

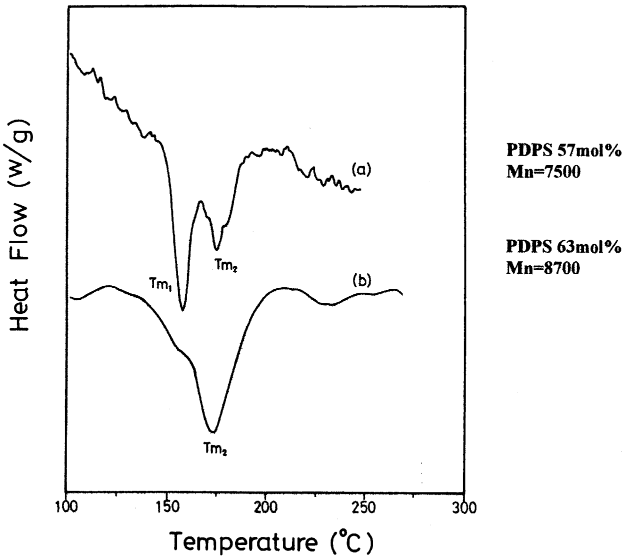

Fig. 9. DSC thermograms of (a) $F_{18}P_{24}$ and (b) $F_{18}P_{30}$ ($F = MeCF_3CH_2CH_2SiO$; $P = Ph_2SiO$).

No regular relationship between T_{m1} and DP_{PDPS} can be found in this series of diblock copolymer samples. However, T_{m2} was found to be a function of both DP_{PDPS} and DP_{PMPS} (Fig. 8). The T_ms of these copolymers are in the range of 102–220°C.

The T_is of those copolymers increase with increasing the degree of polymerization of the PDPS block. The copolymers decomposed before T_i at $DP_{PDPS} \geq 27$.

3.6. PDPS/PMFPS diblock copolymer

Reshuffle side reaction always occurs in synthesizing the PDPS/PMFPS copolymer and causes difficulty in obtaining pre-expected M_n and composition of the copolymer. However, the copolymers with $M_w/M_n \leq 1.28$, $M_n \leq 10.3$k and PDPS ≤ 73 mol% were successfully synthesized through a toluene system (with ≤1 wt% DMSO) and will be studied in this work.

Fig. 9 is the representative DSC thermograms of this copolymer series. Fig. 10 shows the critical composition in relation to the behavior of the T_ms. The copolymers with either a PDPS content higher than 67 mol%, such as F_9P_{24}, $F_{12}P_{24}$, and $F_{15}P_{30}$, or a longer PDPS segment such as $F_{18}P_{30}$ (63 mol%), and $F_{21}P_{30}$ (59 mol%), have a single peak T_m transition. No mesophase transition exits in copolymer with a PDPS content lower than 40 mol% or a shorter PDPS segment (i.e. DP ≤ 12). The copolymers with T_{m2} only almost decomposes before T_i (Fig. 11). The T_ms of these copolymers were found to be within a range of

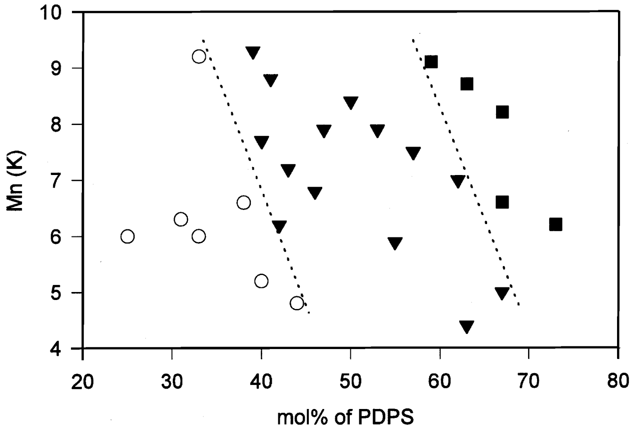

Fig. 10. The critical compositions of PFMPS/PDPS diblock copolymers for the appearance of T_{mi} (▼ with T_{m1}/T_{m2}; ■ with T_{m2} only; ○ without T_{mi}).

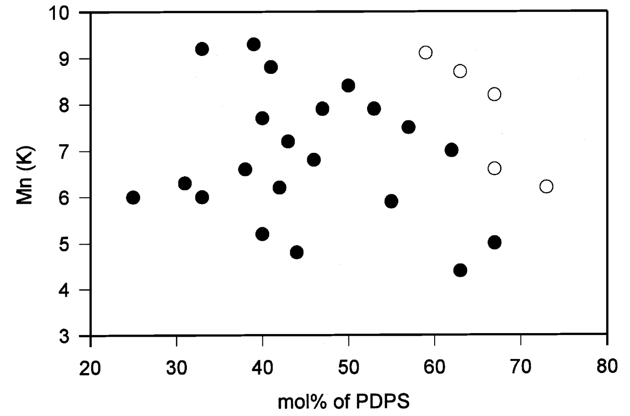

Fig. 11. The critical compositions of PFMPS/PDPS diblock copolymers for the appearance of Ti (● with Ti; ○ without T_i).

125–189°C. T_m as a function of PDPS mo1% is shown in Fig. 12.

4. Conclusions

PDPS/PDMS, PDPS/PMPS and PDPS/PMFPS diblock copolymers, with controlled composition and narrow molecular weight distribution, were synthesized and characterized. The observations of DSC and POM were combined to determine the actually thermal transition behaviors. The critical composition for the mesophase formation as well as the effects of the soft segmental structure on the phase transition behaviors has been demonstrated.

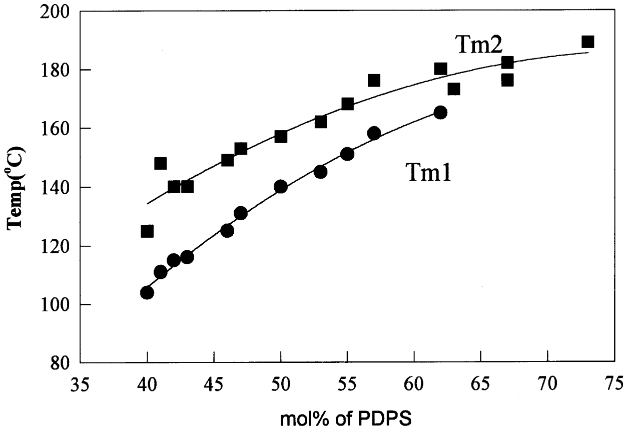

Fig. 12. T_m as a function of PDPS mol% in the PMFPS/PDPS diblock copolymers.

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