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Low-temperature behavior of deswollen poly(dimethylsiloxane) networks

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Abstract

Low-temperature behaviors such as glass transition, crystallization and crystalline melting for deswollen poly(dimethylsiloxane) (PDMS) networks were investigated by differential scanning calorimetry (DSC) as a function of polymer volume fraction at preparation (ϕ). The deswollen networks were made by removing the solvent from the PDMS gels prepared in solutions. For the gels prepared at low ϕ, much loss of the solvent in deswelling causes large decrease of the gel volume, which is expected to result in supercoiling, i.e. to make conformation of the network chains more compact relative to random-coil. The deswollen networks of high ϕ ($\geq$0.44) showed neither the crystallization nor the melting-recrystallization behavior during heating process while the precursor linear PDMS did, which suggests that introduced crosslinks and trapped entanglements are against crystallization. Thermal behavior for modest low ϕ ($\approx$0.2) was similar to one of the precursor linear PDMS due to reduction in trapped entanglements by crosslinking at the low polymer concentration. In spite of smaller number of trapped entanglements, the deswollen networks of the lower ϕ ($\leq$0.14) showed neither the crystallization nor melting-recrystallization. The ϕ dependence of degree of crystallinity had a maximum at $\phi \approx 0.2$, and the values for $\phi \leq 0.14$ were definitely smaller than the maximum value. The anomalies for the ϕ dependence of thermal behavior and the degree of crystallinity in $\phi \leq 0.14$, strongly suggests formation of a considerably shrunken conformation (supercoiling) which inhibits the crystallization and the melting-recrystallization during heating process, and depresses degree of crystallinity. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Deswelling; Differential scanning calorimetry; Supercoil

1. Introduction

Statics and dynamics of polymer chains with some more compact conformations relative to random-coil have been a subject of great interest from theoretical viewpoints [1]. Such a shrunken conformation can be formed under some external constraints or by some strong intra-molecular interactions. *Deswollen* polymer networks have been assumed as one of the systems composed of polymeric chains with such a collapsed conformation [2–5]. The deswollen polymer networks are dry networks made by removing solvents fully from polymer gels prepared in solutions. When polymer concentration of the solution for gel preparation is low, large decrease in the gel volume occurs in deswelling due to much loss of the solvent. Dimension of the network chains should be significantly reduced according to decrease in the macroscopic volume of gel. The resulting shrunken conformation of network chain in the deswollen gels has been historically called *supercoil* to discriminate from random-coil [2–4]. The SANS studies by Bastide et al. [6–8] on a deswollen polystyrene gel reported that gyration radius of deuterated labeled network chain is smaller than one in the unperturbed state when the labeled path is at least a few times larger than the mesh size, while a rather low variation in gyration radius in deswelling was observed at the level of the mesh size. Their experiments seem to imply that the degree of supercoiling depends on spatial scale. However, it should be noticed that in the case of polystyrene gels, the interpretation of variation of the chain dimensions in deswelling is complicated because the systems changes from rubbery state to glassy state. In such a sense, microscopic characterization for the deswollen network systems remains incomplete as yet. On the other hand, the conformation of network chains in dry rubbery network *cured in the bulk state* should be random-coil, as the SANS studies for a bulk-cured rubbery network [9–12] reported that the gyration radius at the level of the mesh size is comparable to the one in the unperturbed state.

Due to supercoiling of the network chain, physical properties of the deswollen polymer networks have been

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expected to differ from the ones of as-prepared gels and dry networks cured in bulk state [2–5]. Vasiliev et al. [13] and we [14] independently reported that polymer concentration dependence of elastic modulus for deswollen polydimethylsiloxane (PDMS) networks strongly deviates from the prediction of classical rubber elasticity theory assuming conformation of network chain as random-coil before and after deswelling. Recently, we have experimentally demonstrated that deswollen PDMS networks made with solutions of low polymer concentrations (ca 10 vol%) reveal remarkable extensibility over 2000–3000% in ultimate strain [14–17]. The high extensibility was considered to result from that the deswollen networks have much lower number of trapped entanglements and smaller end-to-end distance of the network chains in the un-deformed state in comparison with network cured in the bulk state. Trapped entanglements are elastically effective in a similar way as chemical crosslinks are [18,19], which can be an origin of fracture under the ultimate elongation. It should be noticed that both the number of trapped entanglements and the end-to-end distance of network chains in deswollen gels become smaller with decrease in polymer concentration at preparation. Stress–elongation relations of the deswollen PDMS networks with high extensibility were quite different from ones before deswelling, which indicates that conformation of the network chain is significantly different before and after deswelling [14–17]. We evaluated fractal dimension of supercoil from the stress–elongation relation on the basis of Pincus blob concept, and concluded that supercoil is a much more compact conformation than random-coil [14,17].

Details of supercoiled conformation and physical properties of deswollen networks still remain to be elucidated, and they should be investigated from various theoretical and experimental viewpoints. In this study, we have investigated low-temperature behavior of deswollen PDMS networks by differential scanning calorimetry (DSC) as a function of polymer volume fraction at preparation (ϕ). PDMS is highly crystallizable at low temperatures, and the crystallization and glass transition behavior have been studied by several researchers [20–23]. Clarson et al. investigated low-temperature behavior of crosslinked PDMS and the ones reinforced by silica filler particles [23]. They reported that introduction of crosslinks and filler particles into PDMS matrix influenced the crystallization and glass transition behavior of PDMS, which resulted from that mobility of PDMS chains was constrained by crosslinks and filler particles. As degree of supercoiling increases with decrease in ϕ, the ϕ dependence of low-temperature behavior of deswollen networks should provide us with some significant information about the effect of shrunken comformation of supercoil on the mobility of network chains. We show that the ϕ dependence of the crystallization, the melting behavior and the degree of crystallinity show anomalies in low ϕ region, and that the anomalies are experimental evidences for supercoiling.

2. Experimental

2.1. Sample preparation

Vinyl-terminated PDMS of $M_n = 8.4 \times 10^4$ and $M_w/M_n = 1.28$ was used as bi-functional precursor chain where M_n and M_w are number- and weight-average molecular weight, respectively. The PDMS was obtained by fractionation of commercial PDMS (FM-2241, Chisso Co.) with a mixture of methanol and methylethylketone. The PDMS was dissolved in distilled toluene, and the solutions with a series of volume fraction of PDMS were used for preparation of the PDMS gels. The PDMS was crosslinked by end-linking reaction. The end-linking reaction was carried out by hydrosilylation at 75°C for 3 days in a sealed tube. Tetrakisdimethylsiloxysilane and $H_2PtCl_6 \cdot 6H_2O$ were used as tetra-functional crosslinker and catalyst for hydrosilylation, respectively.

The resulting gels were immersed in toluene for 1 week to remove un-reacted materials. The toluene was renewed everyday. Deswelling was gradually made by using mixtures of methanol (poor solvent for PDMS) and toluene with a series of composition as swelling agents. Content of methanol in the mixture was gradually increased, after quasi-equilibrium swelling in a mixture with each composition was experimentally checked. After deswelling in 100% methanol solvent, the gels were completely dried in air. Fractions of un-reacted PDMS were evaluated from sample weights in the dry state. Volume fractions of PDMS incorporated into polymer network at preparation (ϕ) were re-calculated by subtracting the fractions of un-reacted PDMS from the PDMS fractions at preparation.

2.2. DSC measurements

DSC measurements were made after cooling at two different cooling speeds, 9 and 200°C min^{-1}, using Rigaku DSC8230B and Perkin–Elmer DSC7, respectively. Samples

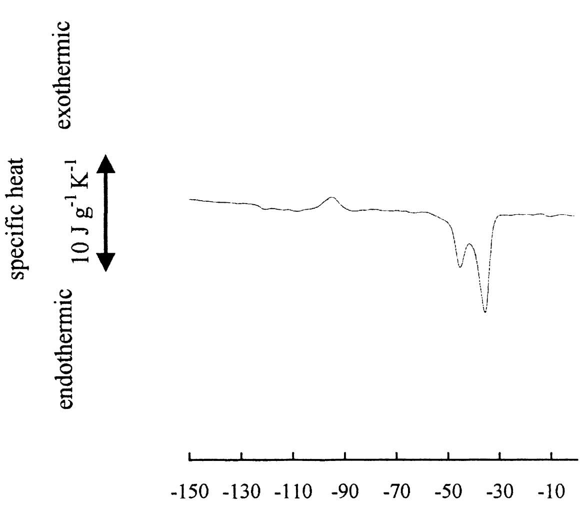

Fig. 1. Specific heat vs. temperature curve of the precursor linear PDMS after 9°C min^{-1} cooling.

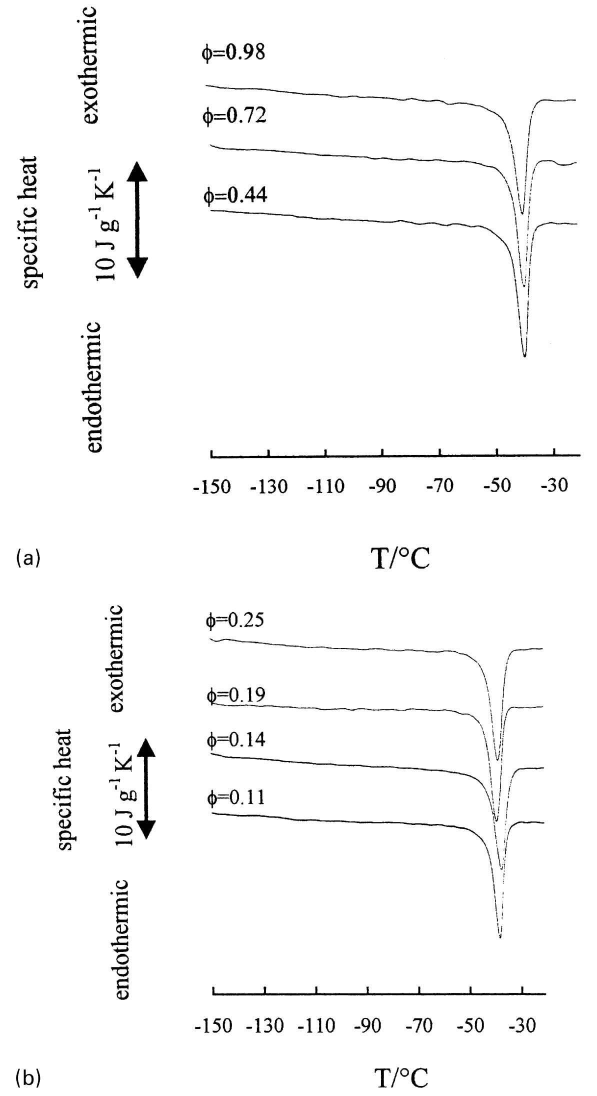

Fig. 2. Specific heat vs. temperature curves of deswollen PDMS networks after 9°C min^{-1} cooling: (a) $\phi \geq 0.44$ and (b) $\phi \leq 0.25$.

weighing ca 10 mg were placed in aluminum DSC pans. The samples were cooled to −150°C from room temperature, and then, heated at 5 and 10°C min^{-1} for the slowly and rapidly cooled samples, respectively. Heats of fusion were calculated from peak areas for crystalline melting in the DSC thermograms.

3. Results and discussion

Figs. 1 and 2 show specific heat vs. temperature curves of the precursor linear PDMS and the deswollen PDMS networks with a series of ϕ after cooling at 9°C min^{-1}, respectively. The sample of $\phi = 0.98$ corresponds to the bulk-cured one, and 2 vol% is the fraction of the unreacted materials. All the network samples show single endothermic crystalline melting peak without appreciable glass transition, while the linear PDMS shows single exothermic peak for crystallization and double melting peaks together with glass transition around −125°C. Except for no appreciable glass transition for the network samples, the thermograms are qualitatively similar to the ones for an uncrosslinked and the bulk-crosslinked PDMS after cooling at 49°C min^{-1} reported in an earlier study [23]: crystallization peak is not observed in the PDMS networks, while it is in the linear PDMS; crystalline melting peak is single and double in the PDMS networks and the linear PDMS, respectively. Clarson et al. attributed the differences to inhibiting effects of junction points on crystallization and melting-recrystallization of small and imperfect crystallites [23]. The double melting peak has been variously interpreted as reorganization of small and imperfect crystallites during heating process [21,23], or as melting of different two crystal forms of PDMS [20,22], although only one type of crystal structure has been reported for linear PDMS [24]. Clarson et al. considered that the double melting peak originates from melting-recrystallization because introduction of crosslinks into PDMS matrix changes the double melting peak into the single one [23]. They observed a glass transition temperature around −120°C for the PDMS networks after cooling at 49°C min^{-1}. Helmer et al. reported that linear PDMS slowly cooled at 1°C min^{-1} does not show glass transition due to the high crystallinity [20]. No appreciable glass transition in Fig. 1 is attributable to the slow cooling rate, though the cooling rate 9°C min^{-1} is larger than their reported value of the minimum cooling rate for detecting T_g of linear PDMS. The minimum cooling rate for detecting T_g of crosslinked polymer would be higher than the one of the un-crosslinked polymer due to lowering effects of the junction points on mobility of network chains.

Table 1
Number-average molecular weight (M_n), glass transition temperature (T_g), crystalline melting temperatures (T_m), enthalpy of fusion (ΔH_m) for the precursor linear PDMS

M_n	T_g (°C)	T_m (°C)	ΔH_m J^{-1} g^{-1}
8.4×10^4	124.2	45.1, 35.3	35.6

Tables 1 and 2 summarize glass transition temperatures

Table 2
Incorporated polymer volume fractions at preparation (ϕ), glass transition temperatures (T_g), crystalline melting temperatures (T_m), enthalpies of fusion (ΔH_m) for the deswollen PDMS networks after 9°C min^{-1} cooling

ϕ	T_g (°C)	T_m (°C)	ΔH_m J g^{-1}
0.98	–[a]	−38.7	29.8
0.72	–	−38.5	29.6
0.44	–	−38.4	30.6
0.25	–	−39.2	33.2
0.19	–	−40.3	33.2
0.14	–	−37.8	29.4
0.11	–	−38.9	29.9

[a] Not detected.

(T_g), crystalline melting temperatures (T_m) and heats of fusion (ΔH_m) for the precursor PDMS and the deswollen PDMS networks after cooling at 9°C min^{-1}, respectively. The values of T_g, T_m, ΔH_m for the precursor PDMS and T_m, ΔH_m for the bulk-cured network ($\phi = 0.98$) are close to the reported values [21–23], respectively. It is seen that T_m and ΔH_m for the deswollen networks are smaller than the ones for the precursor PDMS. The junction points act as defects for crystallization, and thus depress T_m and degree of crystallization, namely, ΔH_m. Although T_m does not appreciably depend on ϕ, the ϕ dependence of ΔH_m is complicated but interesting, which will be discussed later together with results for rapidly cooled samples.

Table 3
Incorporated polymer volume fractions at preparation (ϕ), glass transition temperatures (T_g), crystalline melting temperatures (T_m), enthalpies of fusion (ΔH_m) for the deswollen PDMS networks after 200°C min^{-1} cooling

ϕ	T_g (°C)	T_m (°C)	ΔH_m J g^{-1}
0.98	120.6	−41.5	29.1
0.72	121.5	−42.7	28.4
0.44	120.7	−41.7	30.9
0.25	120.7	−45.3, −39.6	32.9
0.19	120.1	−46.9, −40.8	37.2 (34.7)[a]
0.14	121.2	−42.3	28.7
0.11	121.2	−42.8	29.3

[a] Contribution of crystallization during heating is subtracted.

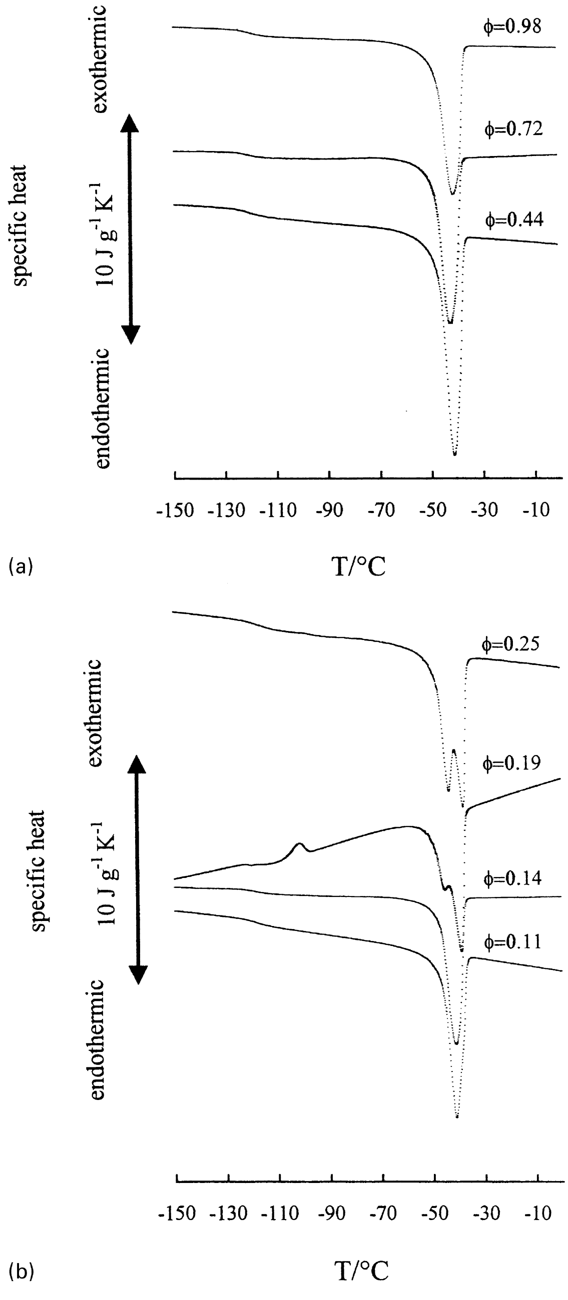

Fig. 3. Specific heat vs. temperature curves of deswollen PDMS networks after 200°C min^{-1} cooling: (a) $\phi \geq 0.44$ and (b) $\phi \leq 0.25$.

Fig. 3 indicates thermograms for the deswollen PDMS networks after cooling at 200°C min^{-1}. Table 3 summarizes T_g, T_m and ΔH_m for the rapid cooled samples. All the network samples show glass transition around −120°C. The appearance of glass transition is due to lowering of degree of crystallinity by the rapid cooling. Actually, ΔH_m for the samples of high ϕ, which show neither crystallization nor melting-recrystallization behavior during heating process, are slightly lower than the ones after the slow cooling. The values of T_m for the rapidly cooled samples are lower than the ones for the slowly cooled samples, indicating that the crystallites formed by the rapid cooling have smaller size and/or more imperfect structures relative to the ones by the slow cooling. It is also found in Fig. 3 that the thermal behavior above T_g after the rapid cooling significantly depends on ϕ in contrast to the one after the slow cooling. The thermal behavior above T_g for $\phi \geq 0.44$ and $\phi \leq 0.14$ after the rapid cooling (characterized by one melting peak) is essentially same as the one after the slow cooling. On the other hand, in modest low ϕ (≈ 0.2), the thermal behavior is quite different between the slow and rapid cooling: Double melting peaks (for $\phi = 0.19$ and 0.25) and crystallization peak (for $\phi = 0.19$) appears in the case of the rapid cooling. The thermal behavior for the rapidly cooled deswollen network of $\phi = 0.19$ (characterized by double melting and one crystallization peaks) is similar to the one of the precursor linear PDMS. This similarity implies that network chains in the deswollen gel of $\phi = 0.19$ have fairly higher mobility than that in other deswollen gels. The double melting peaks in $\phi = 0.19$, 0.25 are likely to result from high mobility of network chain due to a small number of trapped entanglements which act as defects for crystallization in a similar way as chemical crosslinks do. Overlapping degree of precursor chains in crosslinking, i.e. number of trapped entanglements decreases with decrease in ϕ. The final melting temperatures for $\phi = 0.19$ and 0.25 are higher than T_m for the other network samples (see Table 3), which indicates that the crystallites for $\phi = 0.19$ and 0.25 have more perfect

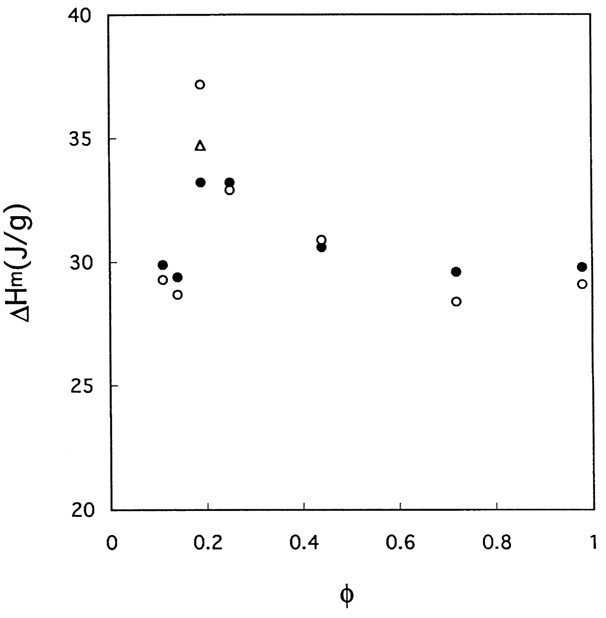

Fig. 4. ϕ dependence of ΔH_m for the deswollen PDMS networks. Closed symbols for cooling rate 9°C min^{-1}, and open symbols for 200°C min^{-1}. Triangular symbol is the data in which contribution of crystallization during heating is subtracted.

structures, and/or have larger size by melting-recrystallization process. The double melting peaks without crystallization peak for $\phi = 0.25$ would imply that crystallization during heating needs higher mobility of network chain than melting-recrystallization. It should be noticed that the network of $\phi = 0.25$ has more trapped entanglements than the one of $\phi = 0.19$.

In $\phi \leq 0.14$, the melting peaks are single (not double), and crystallization peak is not observed. The thermal behavior in $\phi \leq 0.14$ is qualitatively same as the one in high ϕ ($\phi \geq 0.44$) in which mobility of network chain is considerably reduced by topological constraint of many trapped entanglements. The single melting peak and no crystallization peak in $\phi \leq 0.14$ are most probably due to high degree of supercoiling for the network chains. A shrunken conformation of supercoil is presumably disadvantageous to crystallization relative to random-coil conformation. It should be emphasized again that the degree of supercoiling, i.e. decrease of gel volume in deswelling becomes larger with decrease in ϕ, as volume ratio before and after deswelling for a gel prepared at ϕ is approximately given by ϕ. In $\phi \leq 0.14$, the depressing effect of supercoil on crystallizability of network chain would exceed the promoting effect of reduction in trapped entanglements on crystallizability. A deswollen gel with few trapped entanglements which might be prepared around a critical concentration for overlapping of precursor chain (ϕ^*) should be interesting to investigate, but unfortunately, the high conversion of end-linking at such a low polymer concentration ($\phi^* \approx 0.015$ for this system) was not achieved.

The depression effect of supercoil on crystallizability is also recognized in ϕ dependence of ΔH_m as shown in Fig. 4. It is found that ΔH_m increases with decrease of ϕ in $\phi \geq 0.19$, but ΔH_m in $\phi \leq 0.14$ are definitely smaller than the ones in $\phi \approx 0.2$. Such a ϕ dependence of ΔH_m is common to the slow and rapid cooling measurements. The values of ΔH_m for $\phi = 0.19$ after the rapid cooling were calculated by two different ways with or without subtraction of contribution of the crystallization during heating. Initial degree of crystallinity before heating is evaluated by subtracting the peak area of the crystallization from the one of the crystalline melting. The contribution of the crystallization during heating is ca 10% of the total degree of crystallinity. It can be seen that the ϕ dependence of ΔH_m is not essentially influenced by the consideration of the crystallization during heating.

The double melting peaks and the crystallization peak were observed only under the specific condition such as the modest low ϕ and the rapid cooling. They were not seen in any network samples after the slow cooling, and not observed in the network samples with other ϕ after the rapid cooling. The rapid cooling would generate enough amount of amorphous PDMS phase to crystallize during heating, and a considerable amount of small and imperfect crystallites to be melting-recrytallizable during heating. Fairly high degree of mobility for network chains might also be necessary for the emergence of the crystallization and the melting-recrystallization during heating.

It is worth to note that T_g did not appreciably depend on ϕ, and effect of supercoiling on T_g was not clearly observed. Some researchers reported that T_g of crosslinked natural rubbers under a large external constraint such as 200% uniaxial stretching was ca 2°C lower [25], or unchanged [26] in comparison to T_g in the un-stretched state. Their results imply that T_g of rubbery polymer networks might not be so strongly influenced by conformation of the network chains. The effect of shrunken conformation of supercoil on T_g must be so small that it can be within experimental error.

4. Conclusion

Glass transition, crystallization and crystalline melting behaviors of deswollen PDMS networks were investigated by DSC after slow and rapid cooling (9 and 200°C min^{-1}) as a function of polymer volume fraction at preparation ϕ. The thermograms for all the network samples after the slow cooling did not significantly depend on ϕ and they showed only one crystalline melting peak without appreciable glass transition. In the case of the rapid cooling, the thermogram of the modest low ϕ ($\approx$0.2) showed one crystallization and double melting peaks which were not observed for other ϕ, although the glass transition temperatures did not appreciably depend on ϕ. The thermal behavior of the modest low ϕ ($\approx$0.2) was qualitatively similar to the one of the un-crosslinked PDMS, which is due to a considerable reduction in trapped entanglements acting defects for crystallization by the crosslinking at low ϕ. The thermal behaviors of the lower ϕ (≤ 0.14) showed neither the crystallization nor the melting-recrystallization in spite of smaller amount of trapped entanglements. The ϕ dependence of degree of crystallinity had a maximum at $\phi \approx 0.2$ for both the rapidly and slowly cooled samples. The anomalies of the ϕ dependence of the thermal behaviors and the degree of crystallinity in low ϕ are attributable to the formation of a more compact conformation (supercoil) relative to random-coil resulting from large decrease of gel volume in deswelling. The supercoiled conformation is presumably disadvantageous to crystallization relative to the randomcoiled one.

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