Polymer Bulletin 51, 411–418 (2004)
DOI 10.1007/s00289-004-0241-9

Polymer Bulletin

Crystallization and Enthalpy Relaxation of Physically Associating, End-Linked Polymer Networks: Telechelic Pyrene-Labeled Polydimethylsiloxane

Bryce A. Jones[1] **and John M. Torkelson**[1,2](✉)

[1]Department of Chemical and Biological Engineering
[2]Department of Materials Science and Engineering
Northwestern University
Evanston, IL 60208-3120, USA
E-mail: j-torkelson@northwestern.edu

Received: 23 February 2004/Revised version: 1 March 2004/ Accepted: 5 March 2004

Summary

The effects of physical crosslinking or gelation and molecular weight on the crystallization behavior of polydimethylsiloxane (PDMS) are determined by thermal analysis of telechelic, pyrene-end-labeled PDMS and its precursor, telechelic, amine-end-labeled PDMS. The pyrene-end-labeled PDMS forms physical crosslinks while the amine-end-labeled PDMS does not. The presence of physical crosslinks leads to a major reduction in PDMS crystallinity achieved during a 5 °C/min quench that is a striking function of molecular weight. In going from the amine-end-labeled PDMS to the pyrene-end-labeled PDMS, a 25 kg/mol sample exhibits a reduction in PDMS crystallinity from 59% to 30% while a 4-7 kg/mol sample exhibits a reduction in PDMS crystallinity by more than an order of magnitude, from 53% to 2 to 4%, with the latter value depending on the extent of physical crosslinking achieved by the pyrenyl units at the start of the cooling cycle. The PDMS melting temperature is a strong function of physical crosslinking, while the PDMS glass transition temperature is invariant with molecular weight and type of end unit. However, the extent of enthalpy relaxation or physical aging of the PDMS achieved during a brief quench is reduced in the presence of pyrenyl end units and thus physical crosslinking.

Introduction

Model networks of end-linked polydimethylsiloxane chains have been employed for several decades for investigation of important fundamental issues in polymer science. Among these include the role of well-defined crosslinks on elastic modulus and related elastomeric properties as well as equilibrium degree of swelling [1-3]. Significant work has also been done over the past decade in investigating the role of crosslinks, both chemical and physical, on the crystallization of PDMS. In the classical picture of crystallization, the presence of constraints to mobility of the polymer chains is expected to yield a reduced level of crystallinity [4]. A number of studies on PDMS systems support this picture [5-8], including a recent study by Roland and Aronson [5] on chemically crosslinked, end-linked PDMS networks; that study concludes that a network junction precludes approximately eight adjoining PDMS repeat units from being able to crystallize. However, there have also been a couple of reports in opposition to this picture [9,10]. For example, a recent study by Dollase et al. [10] concluded that both chemical end-linking of divinyl PDMS chains and physical crosslinking introduced by including the PDMS chain in an ordered poly(ethylene oxide)-b-PDMS-b-poly(ethylene oxide) triblock copolymer lead to an increased crystallization tendency. They suggested that this effect may be attributed to the enhancement of local ordering, which may facilitate crystallization, in agreement with the conceptual mechanism of "spinodal-like" which indicates that crystallization occurs by cooperative, correlated structural and density fluctuations [11,12].

Given the inconsistent results regarding the impact of chemical and physical crosslinks on PDMS crystallization, we have chosen to examine the crystallization behavior of PDMS in a novel, physically associating, end-linked network made from telechelic, pyrene-labeled polydimethylsiloxane (Py-PDMS-Py). Previous studies on this system have included work by Bright and co-workers [13,14], who used fluorescence to study its cyclization and conformational properties in dilute solution in toluene and supercritical carbon dioxide, and Torkelson and co-workers [15-18], who investigated the behavior of bulk and nanoconfined films of Py-PDMS-Py via fluorescence, differential scanning calorimetry, rheometry, and x-ray scattering. In particular, Jones and Torkelson [18] have recently shown that the bulk Py-PDMS-Py system can yield a physically crosslinked gel as confirmed by rheological characterization when the pyrenyl end units form nanocrystals in the nanoaggregates resulting from the strong insolubility of pyrene in PDMS. (It is noteworthy this strong insolubility of pyrene in PDMS does not allow for the use of the pyrenyl label on the Py-PDMS-Py chain as a simple fluorescence probe of intrinsic, unperturbed polymer behavior as it significantly modifies the behavior of the PDMS, as evidenced by the physical gelation in some Py-PDMS-Py systems. This is in stark contrast to the use of pyrenyl labels in a variety of other polymer systems such as polystyrene and poly(isobutyl methacrylate), where the presence of pyrenyl label at tracer levels does not significantly alter intrinsic polymer properties [19-26].)

Here we report on the crystallization behavior and melting temperature, T_m, of PDMS as a function of both physical crosslinks, formed by the pyrenyl end units that are highly insoluble in PDMS and lead to gelation via pyrenyl unit nanocrystal formation [17,18], and PDMS molecular weight between the pyrenyl end units. Additionally, we employ enthalpy relaxation measurements to comment on the effects of physical crosslinking and PDMS molecular weight on the tendency for physical aging to occur during short-time excursions below the glass transition temperature, T_g, of PDMS in Py-PDMS-Py systems.

Experimental

A detailed description of the synthesis of Py-PDMS-Py and its characterization has been reported [15]. Samples of Py-PDMS-Py were prepared and characterized in manners similar to those described in ref. 15, using 1-pyrenebutyric acid N-hydroxysuccinimide ester (Aldrich) and α,ω-aminopropyl terminated PDMS (NH_2-PDMS-NH_2) (Gelest) as reactants and characterizing the product by ^1H nuclear magnetic resonance (NMR). Based on the use of different molecular weights of NH_2-PDMS-NH_2 and different efficiencies of recovering product after multiple extractions with excess methanol, two different number-average molecular weight samples of Py-PDMS-Py resulted: 7 kg/mol and 25 kg/mol. It should be noted that 4 kg/mol NH_2-PDMS-NH_2 was used to synthesize 7 kg/mol Py-PDMS-Py. It is believed that, after reaction with 1-pyrenebuyeric acid N-hydroxysuccinimide ester to Py-PDMS-Py, low molecular weight portions of the system are lost during methanol extraction resulting in higher molecular weight Py-PDMS-Py samples. This is not seen in the higher molecular weight 25 kg/mol Py-PDMS-Py. According to ^{1}H NMR, within error these samples exhibited full reaction of the pyrenyl dye with the amine end groups, consistent with other studies [13-15] showing that the reaction results in nearly pure Py-PDMS-Py.

Differential scanning calorimetry (DSC) was performed using a Mettler Toledo DSC822 at 5 °C/min heating rates with a nitrogen purge gas and liquid nitrogen as a coolant. In all cases, samples were cooled to -150 °C at a rate of -5 °C/min. Glass transition temperature values reported here are onset values. Values of T_g and T_m have an error of ±0.4 °C associated with them. Enthalpy relaxation values were obtained as the additional area above a hypothetical unaged sample, where there would be no enthalpy relaxation peak. These calculations were performed with the use of software provided with the DSC. Heats of fusion were calculated relative to an indium standard.

Results and Discussion

Figure 1 compares the differential scanning calorimetry thermograms of 25 kg/mol amine-end-labeled PDMS (NH_2-PDMS-NH_2) with 25 kg/mol Py-PDMS-Py upon heating from −150 °C at a rate of 5 °C/min. Several striking differences are observed between the two systems. First, the melting behavior of PDMS is dramatically different; the NH_2-PDMS-NH_2 system exhibits two distinct, endothermic melting peaks while the Py-PDMS-Py system shows a broad melting peaking with a shoulder rather than a second peak. The presence of two melting peaks in the NH_2-PDMS-NH_2 system agrees with results previously obtained in PDMS containing terminal units other than amine groups [8,27,28] and may be ascribed to the recrystallization of metastable crystals which leads to melting at the second, higher melting point. Apparently, this recrystallization process during the heating through the melting regime is significantly impeded by the presence physical crosslinks in the Py-PDMS-Py system, resulting in a reduction of the peak T_m value relative to the higher T_m value in NH_2-PDMS-NH_2 system.

The cold crystallization peak also differs substantially in the two systems, with the Py-PDMS-Py system exhibiting both a reduction in the crystallization temperature and in crystallinity, from 59% to 30%, as compared with the NH_2-PDMS-NH_2 system. These results are also consistent with the results of Roland and Aronson [5] and of Aranguren [8] who studied chemically crosslinked PDMS systems. However, they are inconsistent with the results of Dollase et al. [10] who studied both chemically crosslinked PDMS systems and ordered triblock copolymers containing PDMS middle blocks, the latter yielding a system which may be described as physically crosslinked. The results obtained in the present study are supportive of the notion that constraints

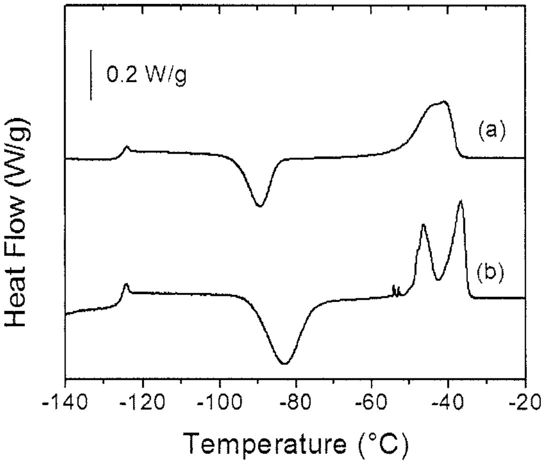

Figure 1: Thermograms showing the glass transition, crystallization, and melting behavior of samples heated from -150 °C: (a) 25 kg/mol Py-PDMS-Py and (b) 25k NH_2-PDMS-NH_2. (Note: A very small level of crystallization of PDMS was observed upon cooling either sample to -150 °C.)

to mobility of polymer chains, such as that provided by physical crosslinks, should yield a reduction in the achievement of crystallization, other things being equal. The crystallization and melting data for the 25 kg/mol Py-PDMS-Py and NH_2-PDMS-NH_2 systems are summarized in Table 1.

Figure 2 compares the differential scanning calorimetry thermograms of 7 kg/mol Py-PDMS-Py with 4 kg/mol NH_2-PDMS-NH_2 from which the Py-PDMS-Py sample was synthesized. (See Experimental for explanation of how the 7 kg/mol sample results from a 4 kg/mol precursor.) The impact of the pyrene end labels on crystallization and melting behavior is much greater in this low molecular weight (MW) system than in the 25 kg/mol system. In order to illustrate more precisely the small crystallization and melting peaks present in the 7 kg/mol Py-PDMS-Py system, the data provided for this system are expanded in Figure 2b. Most notable is the greater than one order of magnitude reduction in the crystallization achieved in the low MW system when the end units are pyrenyl units as compared with amine units. Crystallinity is reduced from 53% in the amine-end-labeled system to 4% in the pyrene-end-labeled system that was quenched from above 40 °C and to 2% in the pyrene-end-labeled system that was quenched from room temperature after being annealed at room temperature for more than 24 hr. The lesser, albeit large reduction in crystallinity in the pyrene-labeled system that was quenched from above 40 °C is due to the fact that this sample began its quench at a temperature above the melting point of the pyrenyl nanocrystals, meaning that the sample was a liquid and not a physically crosslinked gel at the start of the quench. In contrast, the sample that was quenched from room temperature was in a physically gelled state, as defined by rheological measurement [18].

Also notable in Figure 2 are the major reductions, greater than 10 °C, in the crystallization and melting temperatures in the low MW Py-PDMS-Py system relative to the low MW NH_2-PDMS-NH_2 system. All of these results are also consistent with

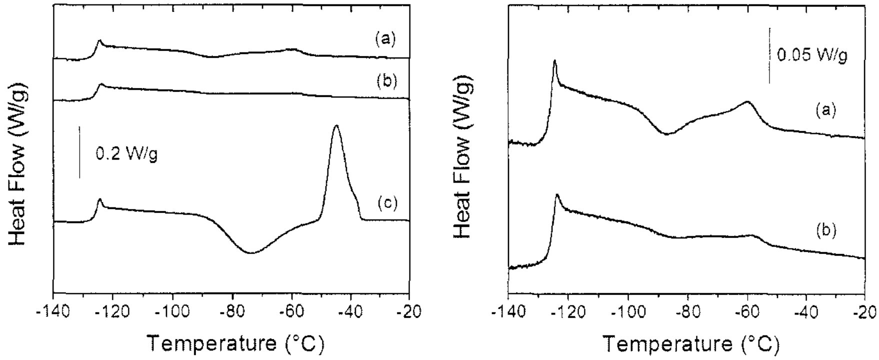

Figure 2a (left) and 2b (right): Thermograms shown upon heating from -150 °C: (a) 7 kg/mol Py-PDMS-Py after heating above 40 °C to remove thermal history and melt pyrene nanocrystals, (b) 7 kg/mol Py-PDMS-Py after annealing at room temperature for more than 24 hr, and (c) 4 kg/mol NH_2-PDMS-NH_2. (Note: A very small level of PDMS crystallization was observed upon cooling any of the samples to -150 °C.)

Table 1: Crystallization and melting data for Py-PDMS-Py and NH_2-PDMS-NH_2 samples

	Onset cryst temp (°C)	Peak cryst temp (°C)	% cryst[1]	Endset melt temp (°C)	Peak melt temp (°C)
25k Py-PDMS-Py	-96.8	-90.6	30%	-38.4	-42.2
25k NH_2-PDMS-NH_2	-92.6	-84.0	59%	-35.7	-47.1, -37.3
7k Py-PDMS-Py[a]	-98.3	-87.9	4%	-54.9	-59.8
7k Py-PDMS-Py[b]	-96.1	-85.6	2%	-54.1	-56.8
4k NH_2-PDMS-NH_2	-87.4	-74.1	53%	-38.9	-45.0

[1] % crystallinity taken from crystallization peak upon heating

[a] Thermal history 1: Py-PDMS-Py heated above 40 °C prior to quench

[b] Thermal history 2: annealed at room temperature for longer than 24 hr

Table 2: T_g and enthalpy relaxation data for Py-PDMS-Py and NH_2-PDMS-NH_2

	T_g	Relaxation enthalpy (J/g)
25k Py-PDMS-Py	-127.8	0.59
25k NH_2-PDMS-NH_2	-127.2	1.03
7k Py-PDMS-Py[a]	-127.3	0.79
7k Py-PDMS-Py[b]	-126.9	0.60
4k NH_2-PDMS-NH_2	-126.7	0.85

[a] Thermal history 1: Py-PDMS-Py heated above 40 °C prior to quench

[b] Thermal history 2: annealed at room temperature for more than 24 hr

the notion that the presence of constraints on chain mobility can lead to both a reduced tendency to achieve crystallization and less perfect crystals that are less able to undergo recrystallization during heating. The near absence of crystallization in the low MW Py-PDMS-Py sample that was cooled from the physically gelled state is also consistent with the results of Aranguren [8] who demonstrated that the complete suppression of PDMS crystallization could be achieved for chemically crosslinked samples of PDMS mixed with fumed silica. The crystallization and melting data for the low MW Py-PDMS-Py and NH_2-PDMS-NH_2 systems are summarized in Table 1.

Careful inspection of Figures 1 and 2 also allows one to comment on the effect of physical crosslinking on the T_g and enthalpy relaxation behavior of PDMS systems; these results are summarized in Table 2. Within error, there is no change in the T_g values of PDMS with MW or physical crosslinking caused by the inclusion of pyrenyl end units. The invariance of T_g with the MWs investigated here is expected based on the fact that the T_g of PDMS has previously been shown to independent of MW when the number average MW exceeds 4 kg/mol [29]. The lack of an effect of physical crosslinking on T_g is also reasonably consistent with the results of Aranguren [8] who reported only a 2 °C increase in T_g upon the chemical crosslinking of PDMS. Figure 2 also indicates a qualitative reduction in the heat-capacity increment at T_g in going from the NH_2-PDMS-NH_2 (with no physical crosslinking) to the Py-PDMS-Py that was first heated to melt the pyrenyl nanocrystallites before cooling (yielding intermediate physical crosslinking) to the Py-PDMS-Py that had been annealed at room temperature for more than 24 hr prior to cooling (yielding high physical crosslinking). This observation is consistent with that found in chemically crosslinked polymers, where the heat-capacity increment is a decreasing function of the density of chemical crosslinks [30], but is opposite to predictions from an energy landscape interpretation of the glass transition [31].

To our knowledge, no study of the effect of chemical or physical crosslinking on the enthalpy relaxation of PDMS has been previously reported. However, there have been studies on the effect of chemical crosslinking on enthalpy relaxation for a variety of epoxy thermosets [32-34], which indicate that at a constant degree of undercooling the extent of enthalpy relaxation decreases as the crosslink density is increased. These results may be explained by the topological constraints to segmental reorganization that are induced by crosslinking; this segmental reorganization is needed to achieve physical aging. While the enthalpy relaxation data obtained in the present study are for only a single cooling rate and heating rate, with no time being spent at constant annealing temperature in the glassy state, the limited results illustrated in Figures 1 and 2 and detailed in Table 2 indicate that, like chemical crosslinking, physical crosslinking leads to a reduced extent of enthalpy relaxation, other things being equal. These results are also consistent with studies [35,36] investigating the impact of chemical crosslinks on physical aging that employ characterization methods other than enthalpy relaxation.

Conclusions

As determined by comparison of the behavior of Py-PDMS-Py and NH_2-PDMS-NH_2 systems, the effect of physical crosslinking on the crystallization and enthalpy relaxation behavior of PDMS is consistent with the picture that the presence of constraints to mobility of polymer chains yields reduced levels of crystallinity and enthalpy relaxation. The effect of physical crosslinking on crystallinity is especially strong in the case of the low MW Py-PDMS-Py systems, where crystallization at a 5

°C heating rate is nearly eliminated, in qualitative accord with the determination by Roland and Aronson [5] that a network junction precludes approximately eight adjoining PDMS repeat units from being able to crystallize. Both the crystallization and melt transition temperatures are significant functions of physical crosslinking, especially in the low MW system, where reductions of 10 °C or more are observed in Py-PDMS-Py relative to NH_2-PDMS-NH_2. In contrast, T_g is invariant with regard to both physical crosslinking and molecular weight in the systems studied here.

Acknowledgements. This work made use of Central Facilities supported by the MRSEC program of the National Science Foundation (Grant DMR-0076097) at the Materials Research Center of Northwestern University. We also acknowledge financial support from Northwestern University.

References

1. Mark JE, Sullivan JL (1977) J Chem Phys 66:1006.
2. Sharaf MA, Mark JE, Ahmed E (1994) Colloid Polym Sci 272:504.
3. Hild G (1998) Prog Polym Sci 23:1019.
4. Armistead K, Goldbeck-Wood G, Keller A (1992) Adv Polym Sci 100:221.
5. Roland CM, Aronson CA (2000) Polym Bull 45:439.
6. Urayama K, Yokoyama K, Kohjiya S (2000) Polymer 41:3273.
7. Patel M, Morrell PR, Skinner AR (2002) Macromol Symp 180:109.
8. Aranguren MI (1998) Polymer 39:4897.
9. Ebengou RH, Cohenaddad JP (1994) Polymer 35:2962.
10. Dollase T, Spiess HW, Gottlieb M, Yerushalmi-Rozen R (2002) Europhys Lett 60:390.
11. Olmsted PD, Poon WCK, McLeish TCB, Terrill NJ, Ryan AJ (1998) Phys Rev Lett 81:373.
12. Strobl G (2000) Eur Phys J E 3:165.
13. Kane MA, Baker GA, Pandey S, Maziarz EP, Hoth DC, Bright FV (2000) J Phys Chem B 104:8585.
14. Kane MA, Pandey S, Baker GA, Perez SA, Bukowski EJ, Hoth DC, Bright FV (2001) Macromolecules 34:6831.
15. Kim SD, Torkelson JM (2002) Macromolecules 35;5943.
16. Jones BA, Kim SD, Guinn L, Torkelson JM (2002) Polym Preprints 43(2): 1339
17. Jones BA, Torkelson JM manuscript submitted
18. Jones BA, Torkelson JM manuscript in preparation
19. Deppe DD, Dhinojwala A, Torkelson JM (1996) Macromolecules 29:3898.
20. Deppe DD, Miller, RD, Torkelson JM (1996) J Polym Sci Part B Polym Phys 34:2987.
21. Hall DB, Dhinojwala A, Torkelson JM (1997) Phys Rev Lett 79:103.
22. Hall DB, Miller RD, Torkelson JM (1997) J Polym Sci Part B Polym Phys 35:2795.
23. Hall DB, Torkelson JM (1998) Macromolecules 31:8817.
24. Hall DB, Deppe DD, Hamilton KE, Dhinojwala A, Torkelson JM (1998) J Non-Cryst Solids 235:2357.
25. Ellison CJ, Torkelson JM (2002) J Polym Sci Part B Polym Phys 40:2745.
26. Ellison CJ, Torkelson JM (2003) Nature Mater 2:695.
27. Helmer JD, Polmanteer KE (1969) J Appl Polym Sci 13:2113.
28. Lee CL, Johannson OK, Flaningam OL, Hahn P (1969) Polym Preprints 10(2):1311.
29. Clarson SJ, Dodgson K, Semlyen JA (1985) Polymer 26:930.
30. Santangelo PG, Roland CM (1998) Phys Rev B 58:14121.
31. Angell CA (1995) Science 67:1924.
32. Cook WD, Mehrabi M, Edward GH (1999) Polymer 40:1209.
33. Hutchinson JM, McCarthy D, Montserrat S, Cortes P (1996) J Polym Sci Part B Polym Phys 34:229.

34. Cortes P, Montserrat S, Hutchinson JM (1997) J Appl Polym Sci 63:17.
35. McCaig MS, Paul DR (1999) Polymer 40:7209.
36. Lindsay GA, Henry RA, Hoover JM, Knoesen A, Mortazavi MA (1992) Macromolecules 25:4888.