Polymer Bulletin 45, 439–445 (2000)

Polymer Bulletin

Crystallization of polydimethylsiloxane end-linked networks

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Received: 31 July 2000/Accepted: 18 September 2000

Summary

End-linked polydimethylsiloxane networks were synthesized, and used to quantify the reduction due to crosslinking of both the extent and thermodynamic stability of the crystalline phase. Networks of varying crosslink density were isothermally crystallized at various temperatures. The consequent melting points were found to be a linear function of the crystallization temperature, enabling equilibrium melting temperatures to be determined by extrapolation. From the dependence of the equilibrium melting point on crosslink density, it was determined that a network junction precludes roughly 8 adjoining chain units from incorporating into the crystal phase. This result is consistent with the measured degree of crystallinity suppression in the networks.

INTRODUCTION

The tethering of polymer chains to form a network affects not only the low frequency dynamics, which is usually the intent, but also other properties such as the viscoelasticity [1-6] and crystallization behavior [7-9]. Crosslinking reduces both the extent and stability of the crystalline phase. The network junctions *per se* can not crystallize, and moreover they constrain topologically neighboring chain units from incorporating into the crystal phase. This not only suppresses the degree of crystallinity, but also results in a depression of the melting point.

In this note we describe the crystallization behavior of end-linked polydimethysiloxane (PDMS) networks. This material is often used in model studies, for example of structure-property relationships [10,11], rubber elasticity [12-14], adhesion [15], and polymer dynamics [16,17]. We have previously addressed the effect of molecular weight [18,19] and crystallinity [20] on local segmental motion in PDMS. The experiments described herein are part of a broad effort to study the manner in which constraints on polymer chains engender cooperativity of their motion, and thereby influence various physical properties.

EXPERIMENTAL

End-linked networks were prepared by reaction under inert conditions of hydride-terminated PDMS with a slight excess of tetravinylsilane, using chloroplatinic acid hexahydrate (Strem Chemical) as the catalyst. An additional network was synthesized from vinyl-terminated PDMS and tetrakis(dimethylsiloxy)silane, using a platinum-divinyltetramethyldisiloxane complex as catalyst. All reagents were used as received (from Gelest Inc., except as noted).

The PDMS and crosslinker were mixed and cooled in an ice bath prior to addition of 20 µl of a 0.05 *M* solution of the catalyst. This mixture was stirred until a viscosity increased was observed (1-2 minutes), then allowed to stand overnight at room temperature. After 48 hours at 80C *in vacuo*, Soxhlet extraction with hexane yielded clear, colorless films, *ca.* 0.3 mm thick. The networks, and their molecular weight between crosslinks, M_c, are listed in Table 1. The sample designations refer to the number of monomer units between crosslink junctions, equal to $M_c/74.2$.

The films were used without extraction. It has been shown [21] that PDMS networks prepared by hydrosilation have substantial defects (i.e., chain ends and unattached chains) when the precursor molecular weight exceeds about 30,000 daltons. That is the case herein for only the least crosslinked sample (N845). The quantity of extractable material, listed in Table 1, was lower for N127, prepared by end-linking vinyl-terminated PDMS, than for the networks formed from hydride-terminated chains.

Table 1. PDMS Endlinked Networks

network	M_c (daltons)	soluble fraction
N81	5890	0.15
N127	9290	0.03
N231	17100	0.15
N377	28000	0.11
N845	62700	0.18

The melting behavior of the materials was characterized by differential scanning calorimetry (DSC), using a Perkin Elmer DSC 7 with liquid nitrogen cooling, calibrated using the two transitions of cyclohexane. Samples weighing from 6 to 10 mg were enclosed in sealed aluminum pans. After isothermal crystallization at a temperature T_c, they were heated at 10 deg/min to determine the melting point, T_m. In additional experiments, the maximum degree of crystallinity was determined by annealing the networks for extended time periods at temperatures for which the crystallization rate is fastest. The duration of the crystallization was repeatedly incremented, until no further increase in crystallinity was observed during subsequent heating.

RESULTS

The PDMS networks were crystallized at a series of temperatures in the calorimeter, and the melting points obtained on subsequent heating. Shown in the inset to Fig. 1 are representative DSC scans for two networks, crystallized at the same temperature. Since the network junctions act as defects, reducing the thermodynamic stability of the crystalline phase, the more crosslinked PDMS exhibits a lower melting point.

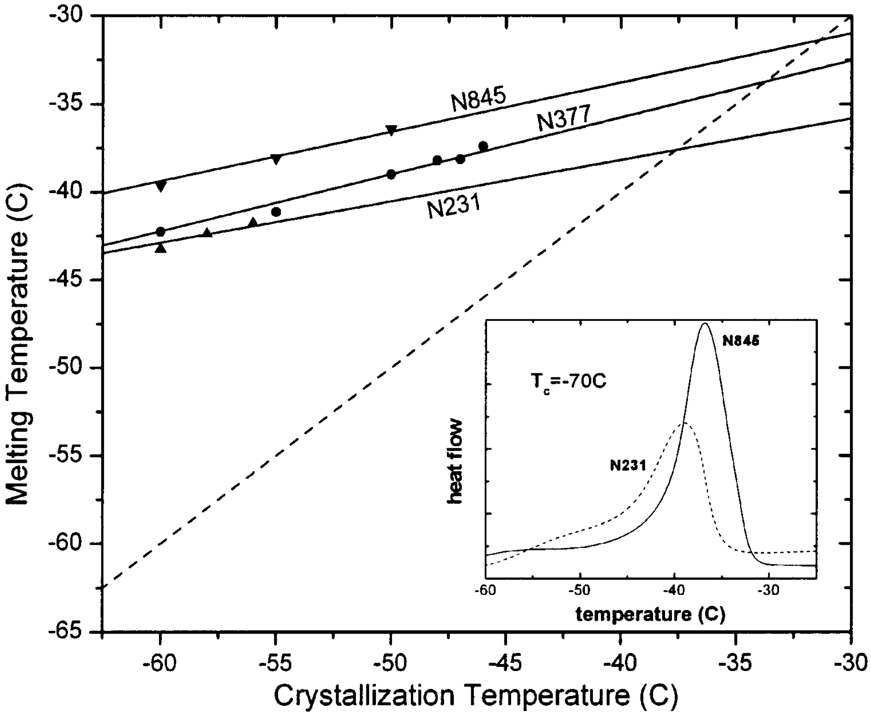

Figure 1. Representative crystallization results for PDMS networks. The equilibrium melting temperature is determined by linear extrapolation to the intersection with the temperature for which $T_m = T_c$ (dashed line). The inset shows the melting endotherm for two networks crystallized at the same temperature.

We quantify this effect by determining the equilibrium melting temperature, T_m^o, which is the hypothetical value for crystals formed under equilibrium conditions. T_m^o for polymers can be determined by a variety of methods, including the use of low molecular weight analogues [22], very slow heating rates [23], and by extrapolating melting temperatures obtained at increasing annealing times [24] or increasingly high crystallization temperatures [25-27]. Herein we use the latter approach, extrapolating the experimental T_m to the value at which it equals the temperature of crystallization; this is taken to be T_m^o [25-27]. The linear extrapolation is based on the assumptions that the fold length of the crystal (growth nucleus) is constant and much less than the other crystallite dimensions, and that no recrystallization occurs during the melting point measurement [25]. Although the analysis considers the most stable crystals, the melting temperature used herein correspond to the onset of the melting endotherm, since this was most accurately determined.

At each T_c, crystallization was permitted to proceed to a measurable extent. Low levels of crystallinity minimize the potential for an increase in crystal fold length, and consequently higher T_m. Displayed in Fig. 1 is a plot of the melting point as a function of crystallization temperature for representative networks. Results for all samples are tabulated in Table 2. The range of temperatures over which data could be obtained decreased with the degree of crosslinking. At higher temperatures crystallization becomes overly slow, while at lower temperatures it is too fast to be executed isothermally.

Table 2. Crystallization Results

PDMS	T_m^0 (C)	maximum crystallinity (%)
N81	–79.2	40.0
N127	–52.8	41.3
N231	–37.6	46.9
N377	–33.7	47.3
N845	–31.4	48.4

Each network was annealed for extended duration at various temperatures, in order to determine the maximum level of crystallinity. The highest degree of crystallinity achieved for each network is listed in Table 2, expressed as mass percent crystallinity, using 61.3 J/g as the perfect heat of fusion for PDMS [28, 29].

ANALYSIS

Network formation not only reduces the quantity of the crystalline phase, it also suppresses it stability. The consequent melting point depression for random crosslinking is related to the fraction, *f*, of uncrosslinked chain units as [7, 30]

$$\frac{1}{T_{\mathrm{m}}^{\mathrm{o}}}-\frac{1}{T_{m}^{\infty}}=-\frac{\mathrm{R}}{\mathrm{H_f}}\ln(1\text{-f}) \tag{1}$$

where R the gas constant and T_m^4 the equilibrium melting point for uncrosslinked PDMS. Strictly speaking, this equation is for random crosslinking, which perturbs the crystallinity more than would end-linking [7, 30].

Applying eq. 1, various investigators have found that melting point depressions measured for various polymer networks exceed the predicted magnitude [9, 31-33]. The reason for this is that a portion of any network chain adjacent to a junction will also be prevented from crystallizing. This will result in a suppression of the crystal phase stability, and thus T_m^o, beyond that due to the truncation of crystallizable sequence lengths by the junction *per se*. In consideration of this, eq. 1 is modified [9]

$$\frac{1}{T_{\mathrm{m}}^{\mathrm{o}}}-\frac{1}{T_{m}^{\infty}}=-\frac{\mathrm{R}}{\mathrm{H_f}}\ln(1\text{-}\xi\mathrm{f}) \tag{2}$$

where > represents the number of chain units precluded from crystallizing per crosslink site. Thus, >*f* is the fraction of the units prevented from crystallizing by virtue of their proximity to a junction.

We fit eq. 2 to the experimental results for the PDMS networks by variation of the parameter >. For T_m^4 we use –29.6C, obtained by extrapolation of melting point data for high molecular weight, linear PDMS to the value at which $T_m=T_c$. The calculation for $\xi = 35$ is shown in Fig. 2. Except perhaps at the highest crosslink densities, good agreement with the experimental results is obtained, implying the existence of *ca.* 35 non-crystallizable chain units per crosslink; that is, the tetrafunctional junctions constrain on the average 8 to 9 adjoining units from incorporation into the crystal phase.

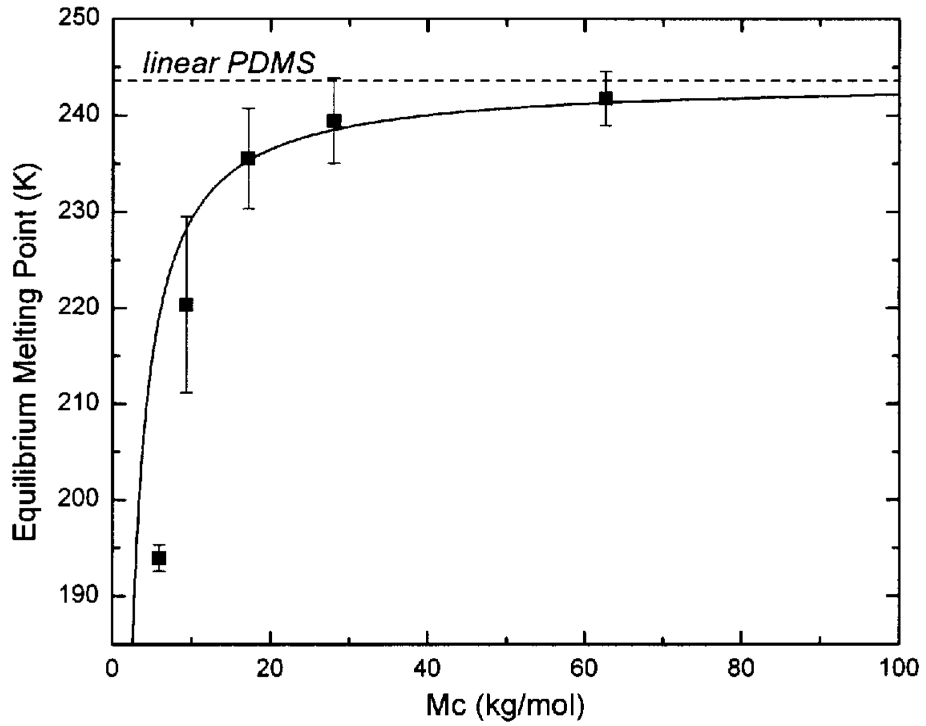

Figure 2. T_m^4.from extrapolation of DSC data (+) and calculated from equation 2 using the best-fit value of ξ=35 (—).

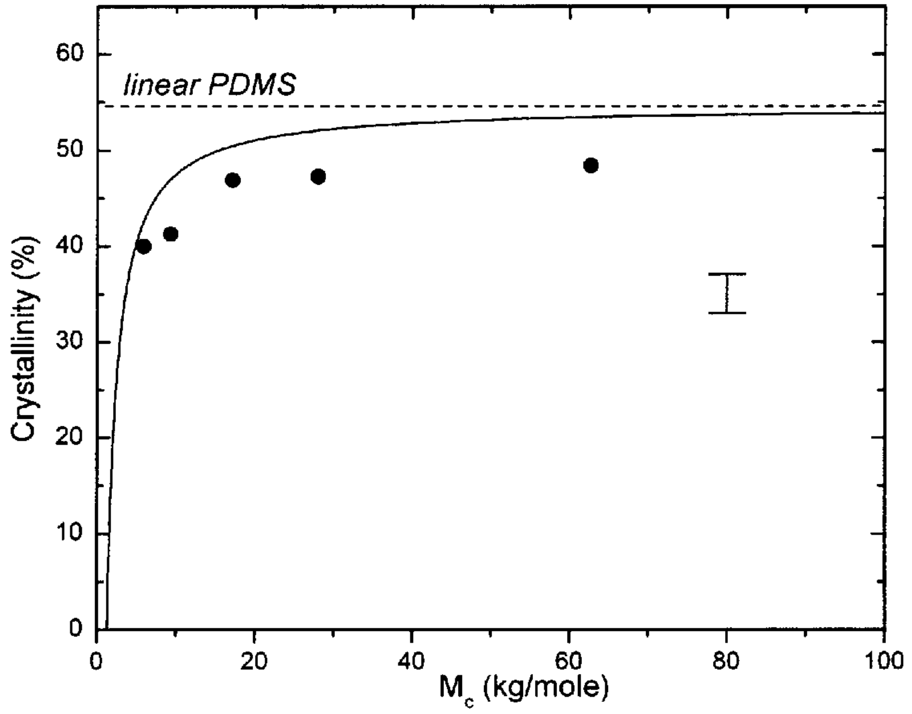

Figure 3. Degree of crystallinity measured for PDMS networks (•), along with the values calculated from the melting point depression (—).

The suppression of crystallization due to constraints imposed by the network junctions should also be reflected in the degree of crystallinity. However, as seen in Table 2, crosslinking has a less marked effect on the degree of crystallinity than on the melting point of the crystals. From the fraction of non-crystallizing chain units deduced from the melting point depression, a prediction of the dependence of the degree of crystallinity on M_c can be made. We assume that the degree of crystallinity of crosslinked PDMS is proportional to that measured for the linear polymer, with the proportionality constant equal to the fraction of crystallizable chain units in the network, which is just the quantity 1 - >*f*. As seen in Figure 3, although the degree of crystallinity is somewhat overestimated, there is qualitative agreement with the experimental results. This is satisfactory, given the absence of any adjustable parameters.

CONCLUSIONS

The formation of a PDMS network inhibits the crystallization of chain units in proximity to the crosslinks. From the depression of the melting point, we estimate that the suppression extends roughly 8 chain units away from a network junction. This value is qualitatively consistent with the degree of crystallinity measured for the materials. It is also quite similar to results obtained on end-linked networks of poly(tetramethylene oxide) [9].

A shortcoming of the present analysis is neglect of the chemical effect of the junctions. A lowering of the chemical potential for the amorphous state could in principle lower T_m^o. This would be beyond that accounted for by eq. 2, thus implying the value deduced for ξ is too high. Additionally, any reduction in crystal perfection [7,32,33] will also contribute to a depression of T_m. On the other hand, eq. 1 assumes random crosslinking, which would depress the melting point more than the end-linking used herein.

Acknowledgements. We thank T.M Keller and E.J. Houser for assistance with the network syntheses. CLA is grateful for a National Research Council postdoctoral appointment at the Naval Research Laboratory. This work was supported by the Office of Naval Research.

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