THERMAL CRYSTALLIZATION OF POLYTETRAHYDROFURAN NETWORKS*

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INTRODUCTION

Poly(oxytetramethylene) (or polytetrahydrofuran, PTHF) is often employed as the soft segment in polyurethane and polyester block copolymers, although the homopolymer itself has negligible commercial utility. PTHF rubbers can serve as useful model systems for the study of mechanical and crystallization behavior. The thermodynamic stability of the crystalline state is reflected in the equilibrium melting temperature, T_{mo}. Equilibrium melting refers to the melting of crystals lacking significant interfacial energy or internal defects. Approaches for determining T_{mo} include the use of low-molecular-weight analogues[1] or infinitely slow heating rates[2], as well as the extrapolation of melting temperatures obtained at increasing annealing times[3], or increasingly high crystallization temperatures[4–6]. In a crosslinked material, the network junctions are inherent defects, expected to inhibit both the extent and the stability of the crystalline phase. The present work was undertaken to characterize the influence of network structure on the thermal crystallization of PTHF. The influence of the length of network chains and dispersity of this length on the crystallization behavior was examined.

EXPERIMENTAL

The PTHF rubbers were prepared and characterized by Prof. R. S. Stein and Dr. L. Jong[7] of the University of Massachusetts. Various unimodal and bimodal networks formed from linear PTHF of various molecular weights were utilized. An allyl terminated linear polymer, of molecular weight between 2000 to 8550, was crosslinked with a stoichiometric amount of pentaerythritol tetrakis(3-mercapto-propionate) to form the unimodal network. Bimodal networks were prepared by random end-linking linear polymers of molecular weight equal to 990 and 8290 respectively in various proportions. The details of the synthesis and its characterization can be found in Reference 7. Samples herein are referred to by their number-average molecular weight between crosslinks (M_c), with designations for the unimodal networks prefaced by a U, the bimodal by a B, and the linear polymers by an L. To the extent that the end-linking reaction is perfectly executed, the polydispersity of the unimodal networks is equivalent to that of the linear precursor polymer. As determined from GPC, the polydispersity of the latter was in all cases less than 1.3[7].

The melting behavior of the materials was characterized using differential scanning calorimetry (DSC). Most of the data were obtained on a Perkin-Elmer DSC 2 with liquid-nitrogen cooling, while some experiments utilized a Perkin-Elmer DSC 7 with either an intercooler or ice-water cooling. Calibrations were performed daily using the two transitions of cyclohexane for the lower temperature calorimeter and the melting of indium for the DSC 7. The consis-

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* Presented at a meeting of the Rubber Division, American Chemical Society, Washington, D.C., October 9–12, 1990. G.

tency within a given day (*i.e.*, while the calorimeter head was maintained at low temperature) was 0.1° standard deviation.

Samples weighing less than 10 mg were enclosed in sealed aluminum pans. Scanning rates were 10°/min unless otherwise noted. Prior to quenching to a temperature for crystallization, the samples were annealed 5 min at 338°K, above which the stability of the PTHF is uncertain[7]. Experiments utilizing higher melting temperatures gave no indication of any memory effects (*e.g.*, residual nucleation). Quenching from 338°K to the lowest temperature utilized (163°K) required several seconds, as indicated by the ability of the calorimeter to control the furnace temperature.

RESULTS

EQUILIBRIUM MELTING TEMPERATURES

The PTHF rubbers were crystallized at a series of temperatures and the resulting melting points obtained from DSC. An extrapolation of the experimental T_m *vs* the temperature of crystallization, T_c, to the value $T_m = T_c$ is an established method for determination of the equilibrium melting temperature[4–6]. A linear relationship between T_m and T_c is expected provided the fold length of the crystal is constant and much less than the other crystallite dimensions and assuming no recrystallization occurs during the DSC measurement[4]. Each sample herein was allowed to develop a measurable degree of crystallinity (endotherm > 2 J/g) at the chosen T_c. A low level of crystallinity is desirable in order to minimize any isothermal thickening due to an increase in the crystal fold length. Data could be obtained over a 10 to 15° range of T_c's, beyond which the crystallization was either inconveniently slow or too fast to be executed isothermally.

Figure 1 depicts Hoffman–Weeks plots for the various PTHF rubbers. In the spirit of the Hoffman–Weeks analysis[4], wherein consideration is focussed on the most stable crystals, the melting temperature was taken to be that at which the endotherm returns to the baseline. Extrapolation of the T_m *vs.* T_c data in Figure 1 to the $T_m = T_c$ value yields the equilibrium melting point, T_{mo}, for each material. The results of linear least-squares fitting of the higher T_c data are displayed in Figures 1 and 2 and Table I. As expected, for both unimodal and bimodal networks, T_{mo} increases with M_c. There is a systematic increase in the slope in Figure 1 with M_c, indicative of a decreasing edge-free energy in the crystals[4]. The spread between the values for the two network types is probably not experimental scatter but reflects actual effects of the network structure. The melting-point depression is not a unique function of the chemical-crosslink density; evidently the distribution in the length of the network strands influences the melting behavior. The stability of the crystal phase has a more complex dependence on chain length, and its distribution than can be captured by a simple average length between crosslinks as represented by M_c. The lower M_c bimodal networks have higher equilibrium melting temperatures than unimodal networks of similar M_c; this likely reflects the presence of long sequences ($M_c = 8290$) of PTHF in the former. At average strand lengths exceeding 5000, however, the unimodal network, lacking the short ($M_c = 990$) sequences, forms a more stable crystalline phase.

Crosslinking reduces both the extent and stability of the crystalline phase. The network junctions *per se* can not crystallize; moreover, they constrain topologically neighboring chain units from incorporation into the crystal phase. If consideration is given only to the non-crystallizability of the crosslinks, the melting-point depression for random crosslinking is given by[8,9]

$$1/T_{mo} - 1/T_{m\infty} = -R/H_e \ln(1 - f), \tag{1}$$

in which H_e represents the (excess) enthalpy of fusion, R the gas constant, and $T_{m\infty}$ the equilibrium melting point of crystals formed from infinitely long crystallizable sequences. The fraction of chain units that are crosslinked is given by

$$f = m/2M_c, \tag{2}$$

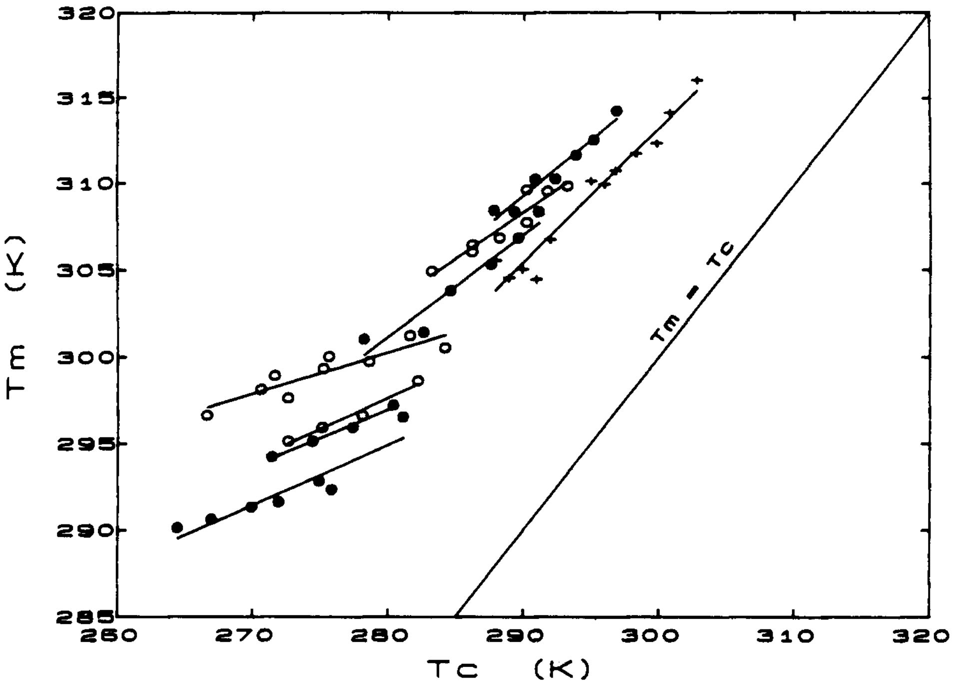

FIG. 1.—The melting points measured for the PTHF rubbers crystallized at various temperatures. The filled and open circles represent data for the unimodal and bimodal networks respectively, while the crosses refer to linear PTHF. The equilibrium melting temperatures determined by linear extrapolation to the intersection with the $T_m = T_c$ line are given in Table I.

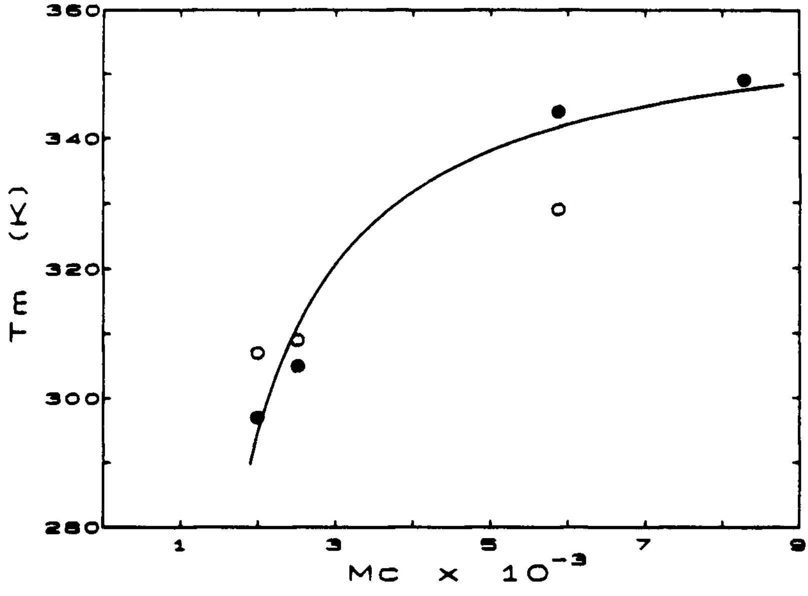

FIG. 2.—The equilibrium melting temperatures for PTHF rubbers of various crosslink density determined from the data in Figure 1. There is no obvious effect of network architecture (unimodal and bimodal represented by filled and open circles respectively). The solid line denotes the dependence of T_m on M_c calculated from Equation (3) using $T_{m\infty}$ = 361°K (obtained from measurements on linear PTHF) and the best-fit value of $\xi = 33$.

TABLE I

THERMAL CRYSTALLIZATION RESULTS

Network	T_m, °K[a]	Heat of fusion, J/g Measured[b]	Heat of fusion, J/g Calculated[c]
U2000	297	42.0	40.
U2520	305	48.6	45.
U5880	344	56.1	61.
U8290	349	57.7	66.
U8550	—	58.1	67.
B2000	307	35.2	40.
B2520	309	41.3	45.
B5880	329	57.3	61.
L8550	361	83.9	—
L10200	—	82.8	—

[a] From Hoffman–Weeks extrapolation.

[b] Equilibrium degree of crystallization at 233°K normalized for the concentration of tetramethylene oxide present. The formula weight of the crosslinkage was 484 g/mol.

[c] Based on the suppression of crystallinity deduced from T_m, using Equation (1) and the best-fit.

where m is the monomer molecular weight. For networks formed by end-linking linear chains, the suppression of the melting point will be less than that for random crosslinking[8]. More important, however, is the neglect in Equation (1) of the reduction in the size and perfection of crystallites formed in crosslinked polymers[9-11]. This will result in a suppression of the crystal phase stability, and thus T_{mo}, beyond that due to the truncation of crystallizable sequence lengths arising directly from the presence of the network junctions.

Experimentally measured melting-point depressions in crosslinked *cis*-1,4-polybutadiene[12], polyethylene[10], and *cis*-1,4-polyisoprene[11] have all exceeded the predictions of Equation (1). Evidently the steric restrictions on the network strands arising from crosslinks suppresses crystallization beyond the junction itself. If it is assumed that the only influence of crosslinking is to restrict some portion of the network chain from incorporation in the crystal, a measure of the extent to which chain units are precluded from crystallization can be obtained from

$$1/T_{mo} - 1/T_{m\infty} = -R/H_e \ln(1 - \xi f) \qquad (3)$$

where ξ represents the number of units prevented from crystallizing per crosslink site. The quantity ξf is the fraction of the chain units prevented from crystallizing by virtue of their proximity to a junction.

Equation (3) can be applied to the experimental results for the PTHF rubbers by taking ξ to be an adjustable parameter. This approach requires knowledge of H_e and $T_{m\infty}$. The perfect heat of fusion of PTHF has been reported to equal 12.4 kJ/mol[13]; this is about 2 kJ/mol smaller than an earlier determination[14]. A value is required for $T_{m\infty}$, representing the equilibrium melting point for PTHF having sequence lengths sufficient to exhibit a melting point independent of chain length.

Linear PTHFs of two molecular weights (8550 and 10 200 respectively) were observed to exhibit equivalent crystallization behavior with respect to both their heats of fusion and their melting temperatures. Consequently, the value obtained by the Hoffman–Weeks procedure for the linear polymers was taken as a measure of $T_{m\infty}$. The equilibrium melting temperature of linear PTHF was found to equal 361°K (Figure 1). This is significantly larger than a value reported for hydroxy-terminated linear PTHF, for which T_m = 321°K for a molecular weight equal to 6760[15]. Results published for linear PTHF of other molecular weights[15-17] are collected in Table II.

Surprisingly, all these previous values for linear PTHF are lower than the T_m determined herein for crosslinked U5880 and U8550. In addition to their shorter sequence length of crystallizable units, upon crystallization, network chains can induce lower entropy configurations in the amorphous phase. These effects hinder crystallization, promoting smaller, less perfect crystals[9-11], and thus the expectation of lower melting points. Since the melting point reflects the stability of the crystalline phase relative to that of the melt, the higher melting points obtained for networks herein compared to published data for linear PTHF may reflect the chemical modification of those chain units which become network junctions. The lower T_m previously found for hydroxy-terminated PTHF[15-17], compared to the present results for either linear or crosslinked PTHF containing pentaerythritol tetrakis(3-mercaptopropionate) or the reaction product of the latter with the allyl end groups, may suggest a significantly lower chemical potential for the amorphous phase of the former.

Using $T_{m\infty} = 361°\text{K}$ and $H_e = 12.4$ kJ/mole, Equation (3) was applied to the equilibrium-melting-point data measured for various crosslink densities by adjustment of ξ. The calculated curve agrees satisfactorily with the experimental data (Figure 2), neglecting any variations in crystal perfection with crosslink density. The best-fit value for ξ provides a measure of the extent to which chain units are precluded from crystallizing. The calculated curve in Figure 2 corresponds to 33 noncrystallizable monomer units per crosslink, which would suggest that the tetrafunctional junctions constrain on the average roughly 8 adjoining units from incorporation into the crystal phase. To the extent that crosslinking reduces the perfection of the crystallites[9-11], this value is an overestimate, although the assumption of random crosslinking underlying Equation (1) perhaps compensates somewhat for this.

ULTIMATE DEGREE OF CRYSTALLINITY

The melting temperature is depressed by the suppression of crystallization due to steric constraints imposed by the network junctions. It is of interest to compare the extent of crystallization suppression (as embodied in the value of ξ deduced from melting-point depression) with the actual degree of crystallinity measured in the crosslinked rubbers. Samples were annealed at 233°K until the level of crystallinity became invariant. This required as much as 2 h for the more highly crosslinked PTHF. The results are displayed in Figure 3 and Table I, wherein a small correction to the measured melting enthalpies has been made to account for the weight of the pentaerythritol tetrakis(3-mercaptopropionate) crosslinker.

From the fraction of noncrystallizing chain units deduced from the melting-point depression, a prediction of the dependence of the degree of crystallinity on M_c can be made. It is assumed that the degree of crystallinity of crosslinked PTHF is proportional to that measured for the linear polymer, with the proportionality constant equal to the fraction of chain units in the network able to crystallize as given by the quantity $1 - \xi f$. As seen in Figure 3, despite the absence of any adjustable parameters, there is acceptable agreement between the extent of crystallization predicted in this manner and the experimentally measured crystallinities.

TABLE II

EQUILIBRIUM MELTING POINTS FOR LINEAR PTHF

Molecular weight	T_m, °K	Method	Reference
3 000	327	Hoffman-Weeks	16
6 760	320	Hoffman-Weeks	15
8 551	361	Hoffman-Weeks	This work
130 000	324	Hoffman-Weeks	15
230 000	343	Asserted	17

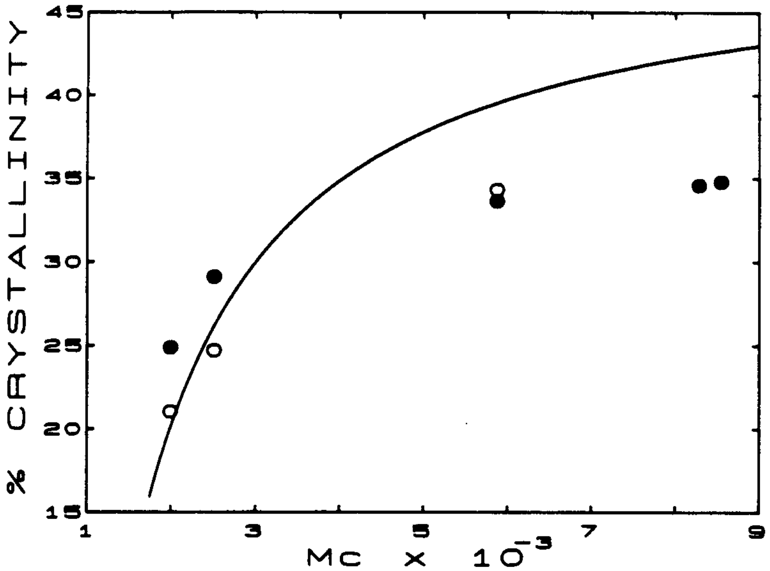

FIG. 3.—The dependence on crosslink density of the equilibrium degree of crystallinity (crystallization temperature equal to 233°K), using 170 J/g as the perfect heat of fusion[13]. The symbols are as defined in Figure 2. The curve represents the crystallinity predicted from the measured melting-point depressions (*i.e.*, $\xi = 33$).

MULTIPLE ENDOTHERMS

After prolonged storage (>6 months) at room temperature (*circa* 296°K) no crystallization of the highly crosslinked networks (*i.e.*, U2000, B2000, and U2520) was observed, while PTHF rubbers with lower crosslink densities exhibited multiple melting peaks after such annealing. The extent of crystallization measured for U5880 and U8550 after various crystallization times are displayed in Figure 4. After one day, both exhibited two melting en-

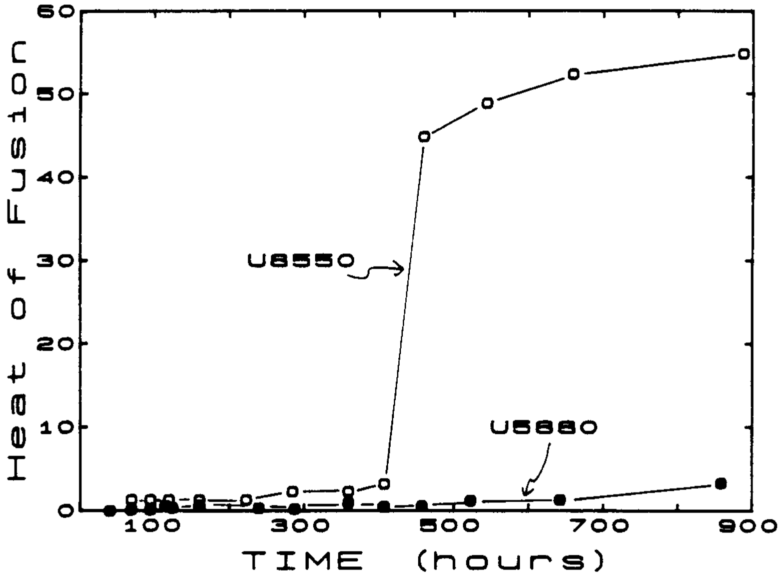

FIG. 4.—The crystallization at room temperature of two PTHF rubbers with unimodal network structures. The ordinate scale is in J/g.

dotherms at about 304°K and 312°K respectively. The melting temperatures of the U8550 were slightly higher than those of the U5880 through about 12 days of crystallization, after which the T_m become essentially equivalent. The higher melting temperature does not change during the course of the annealing at 296°K, while the temperature of the lower peak increases during the crystallization. Eventually, the endotherms merge into a single transition at roughly 312°K. Whether this lower temperature endotherm can be associated with hindered interlamellar spherulitic growth[17,18] is speculative. The disappearance of the lower melting peaks after sufficient annealing at these high (relative to T_m) temperatures may reflect rearrangement of such interlamellar crystallites.

In an attempt to assess the influence of crystal thickening on the melting behavior, the shape of the melting endotherm obtained after annealing at room temperature was studied as a function of the calorimetric heating rate. With slow heating, metastable crystals conceivably have time to reorganize to a more stable form; thus, the intensity of their melting endotherm may decrease relative to that of the more stable form[19-21]. For U5880, however, the effect of changes in heating rate provides no indication of reorganization of metastable crystals to a more stable form (Figure 5).

It is seen in Figure 6 that at sufficiently slow heating rates, U8550 exhibits three melting endotherms. At higher rates of heating, the lowest melting peak disappears, suggesting that it may represent crystalline entities formed during the course of the calorimetry. The intermediate peak in the U8550 data of Figure 6 responds to changes in heating rate in a manner consistent with a metastable crystalline form. It exhibits a melting-point increase with both higher heating rate and prolonged annealing at 296°K.

Coincident with this increase in T_m during annealing, there occurs a substantial increase in the extent of crystallinity for the U8550 after 15 days (Figure 4). The heat of fusion increases from 2 J/g to 45 J/g over 2 days time. An induction period followed by rapid crystallization suggests a homogeneous crystallization process. The glass-transition temperature of linear PTHF is 111° below room temperature[13,22]; accordingly, at room temper-

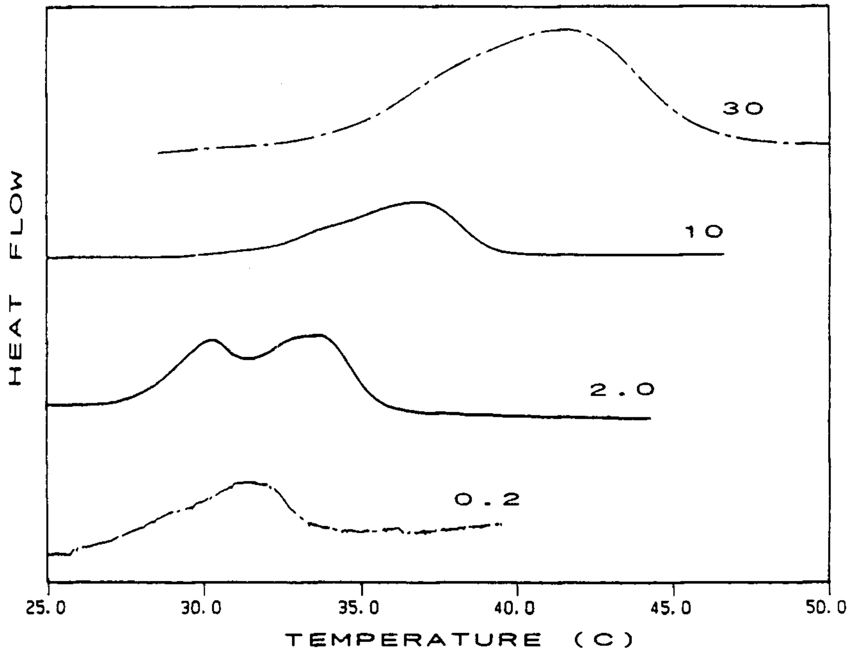

FIG. 5.—Calorimetry results at the indicated heating rates (in degrees per min) for U5880 annealed several weeks at 296°K.

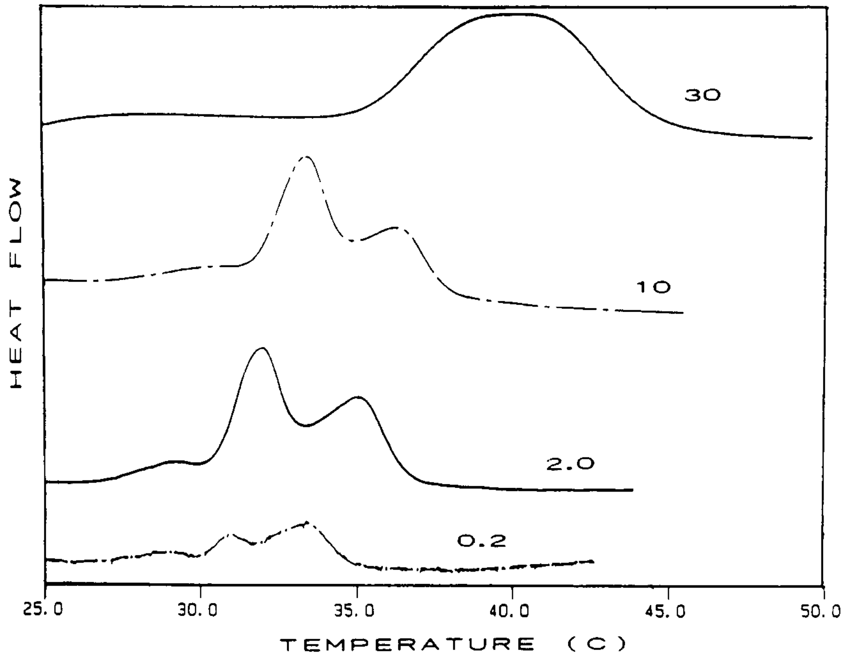

FIG. 6.—Calorimetry results at the indicated heating rates (in degrees per min) for U8550 annealed several weeks at 296°K.

ature, minimal kinetic hindrance of crystallization is expected. The small undercooling at a temperature close to the melting point presumably suppresses spherulite nucleation. The behavior of U8550 in Figure 4 reflects a slow nucleation process preceeding rapid growth of the crystalline phase.

The near cessation in the crystallization of U8550 after roughly 2 weeks at 296°K probably evidences impingement between neighboring spherulites, as has been directly observed in linear PTHF[17,18]. The smaller spherulites associated with a lower temperature of crystallization would presumably allow a greater extent of crystallization before such impingement. The higher degree of crystallinity attained by U8550 at 233°K (Table I) is consistent with such a presumption.

SUMMARY

The formation of a network in PTHF inhibits the crystallization of chain units in proximity to the crosslinks. From melting-point-depression measurements, it is estimated that the suppression in crystallizability extends to as much as 8 chain units away from a network junction. This estimate is consistent with the degree of crystallinity measured in various crosslinked PTHF rubbers.

The equilibrium melting point for linear PTHF was determined to be 361°K. Although this is significantly higher than previously reported values, the present result is congruent with the melting temperatures measured for crosslinked PTHF, and its use leads to satisfactory predictions of their melting-point depression.

The distribution in the lengths of network chains exerted a trivial influence on thermal crystallization behavior. Although this distribution must in principle influence crystallization behavior in so far as it governs crystallizable sequence lengths, differences between uni- and bi-modal network architectures were moderate under the present experimental conditions.

ACKNOWLEDGMENTS

The PTHF networks were prepared and kindly provided by Prof. R. S. Stein and Dr. L. Jong of the University of Massachusetts, with whom beneficial discussions are gratefully acknowledged. This work was supported by the Office of Naval Research.

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