Melting Temperature of the n-Alkanes and the Linear Polyethylenes

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ABSTRACT: The melting behavior of n-alkanes up to carbon number 390 and molecular weight fractions of linear polyethylene up to M_n = 5600 have been analyzed. Surprisingly, it is found that the melting temperature–molecular weight relation is the same for both types of chain molecules. The results are explained in terms of premelting of the n-alkanes, with the disordering of sequences of end units, so that the structure prior to melting is the same as that of the polymer. Support of this conclusion is given by theoretical considerations and experimental results. The difficulties in extrapolating the present data base to the equilibrium melting temperature of the infinite molecular weight chain are discussed.

Introduction

The recent synthesis of high molecular weight n-alkanes,[1-5] with carbon numbers ranging from 102 to 390, has provided a set of model compounds that allow for further study of the crystallization behavior of chain molecules. In addition to the inherent interest in these compounds themselves, they also serve as a bridge between the crystallization of low molecular weight species and fractions of linear polyethylene. In the former case molecular crystals can form, while this type of crystallite is restrained from forming in the polymer.[6] The close connection between the two species is demonstrated by the fact that the molecular weight at which folding can occur, for crystallization either from the bulk or from dilute solution, is the same for the n-alkanes and the polymer fractions.[5,7-13] For example, for linear polyethylenes with molecular weights equal to or less than M_n = 2221, M_w = 2496, that are crystallized from the pure melt, crystallites are formed whose thicknesses are comparable to the extended chain length under all crystallization conditions.[10,13] However, for a slightly higher molecular weight, M_n = 3796, M_w = 4116, crystallites with thicknesses smaller than the extended molecular length are formed at lower crystallization temperatures. At elevated crystallization temperatures extended-chain crystallites are formed. A similar molecular weight demarcation is found in the n-alkanes.[4,7] When crystallized from the pure melt, $C_{192}H_{386}$ (M = 2688) only forms extended-chain crystallites. In contrast, $C_{216}H_{434}$ (M = 3024) can also develop a folded-chain crystallite, depending on the crystallization temperature.[5,14] Thus, folded crystallites can form in both the n-alkanes and the polymers species at comparable molecular weights when crystallized from the pure melt.

A similar situation is found for crystallization from dilute solution. In this case, polyethylene fractions with M_n = 1586 can form either a folded- or extended-type crystallite, depending on the crystallization temperature. At lower molecular weights only extended-chain crystallites form. For M_n = 2859 and greater, only a folded-type crystallite can be developed.[8,9] For crystallization from dilute solution a folded-type crystallite can be developed for $C_{150}H_{302}$ (M = 2100). Although the molecular weights are slightly different between bulk crystallization and dilute solution, there is almost quantitative agreement between the n-alkanes and the polyethylene fractions with respect to the molecular weight at which nonextended crystallite structures can be developed. This conclusion should not be confused with the well-known result that as the chain length of a polymer increases, some type of folded structure will develop. The important distinction being made here is that not only does folding occur in the n-alkanes but it does so at the same molecular weight as is found for linear polyethylene fractions under comparable crystallization conditions.

A variety of studies of the properties of the high molecular weight n-alkanes have recently been reported. These include nucleation theory[9,15,16] morphology,[7,17-19] crystallization kinetics,[16,20,21] and a detailed study of the fusion of dononacontahectane, $C_{192}H_{386}$.[16] The melting points of many of the high molecular weight n-alkanes have been reported in connection with the description of their synthesis and properties.[3,5,7] Melting points have also been reported for low molecular weight fractions of linear polyethylene.[10,13,22] In the present paper we focus attention on a comparison of the melting temperature as a function of chain length of these two different classes of chain molecules. It is necessary for this comparison that extended-chain crystallites, where the crystallite thickness is comparable to the chain length, be formed by both the polymers and the n-alkanes. This requirement limits the polymer data to low molecular weight fractions that can be crystallized in such a manner as to ensure that extended-chain crystallites are formed. Similar requirements also hold for the n-alkanes. It has been demonstrated that n-alkanes up to $C_{390}H_{782}$ can be crystallized in extended form. A sufficient set of data that satisfies the necessary conditions already exists in the literature for the polymer[10,13,22] so that the desired analysis can be made.

Experimental Results

Samples. The origin of the samples and their melting temperatures that will be analyzed have already been described in the literature. The data for the n-alkanes, from $C_{102}H_{206}$ to $C_{390}H_{782}$, come from the synthesis of Bidd et al.[3,7] and of Lee and Wegner.[5] Data for $C_{60}H_{122}$ to $C_{160}H_{322}$ also come from Takamizawa et al.[23] The data for $C_{100}H_{202}$ and below come from Flory and Vrij[6] and is based on the compilation given by Broadhurst.[24]

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The data for the low molecular weight polyethylene fractions come from several sources. Fractions with the number-average molecular weights from 3265 to 5320 are from the work of Fatou and Mandelkern and were prepared by column fractionation.[22] Four fractions with M_n ranging from 1586 to 5600 come from ref 10. In this work, one sample, $M_n = 5600$, was obtained from Societe National Elf Aquitaine (SNEA). The other three fractions were prepared by fractional crystallization and the molecular weights were determined by GPC. Six fractions, with M_n ranging from 575 to 2900, come from more recent work.[13] The three lowest molecular weight fractions in this set were prepared by methods previously described and M_n was determined by end-group analysis using high-resolution NMR.[13]

Melting Temperature Determination. Except for the data from ref 22, the melting temperatures of all the samples, both the n-alkanes and the polymer fractions, were determined by differential scanning calorimetry. The specific procedures used and the significance of the observed melting temperatures in terms of the equilibrium conditions will be discussed in more detail below. The melting temperatures of the data from ref 22 were determined by dilatometric techniques. In this procedure, slow heating followed long-time crystallization at an elevated temperature.

Results and Discussion

In order to make the desired comparison between the equilibrium melting temperatures of the n-alkanes and the polymers, it is necessary to ensure that extended-chain crystallites are formed under the adopted crystallization procedures. This requirement has been established for the n-alkanes up to $C_{390}H_{782}$ using either small-angle X-ray diffraction or the Raman longitudinal acoustical mode (LAM).[5,7] In order to develop extended-chain crystals for molecular weights between $M_n = 2900$ and $M_n = 5600$, long-time crystallization is required at high temperatures.[10] For lower molecular weights, extended-chain crystallites can be developed relatively easily.[10] Extended-chain crystallites could not be formed in a fraction $M_n = 8000$ after crystallization at high temperatures over any reasonable time period at atmospheric pressure. Given that extended-chain crystallites can be formed with molecular weights of 5600 and less, it now needs to be established that the determined melting temperatures are of equilibrium significance. The isothermal crystallization and heating procedures adopted for the dilatometric experiments ensure that equilibrium temperatures were obtained for the extended-type crystallites that were initially formed. In contrast, the determination of thermodynamically significant equilibrium melting temperature, for either the fractions or the n-alkanes, is not obvious by the differential scanning calorimetric technique.[25,26]

It has been demonstrated that constant and thermodynamically meaningful melting temperatures are obtained when sample masses of the order of 1 mg or less are used.[25] There is, however, a significant influence of the heating rate on the melting temperature as determined by differential scanning calorimetry. It has been found that heating rates of 1 °C or less give constant melting temperatures which are demonstrated to be the thermodynamically significant ones.[6,25] For example, heating $C_{192}H_{386}$ at a rate of 1 °C/min or less gives a constant melting temperature of 126 ± 0.1 °C. In contrast, the higher heating rates that are conventionally used yield melting temperatures that are almost 2 °C higher. It is therefore necessary that the melting temperature be determined at, or extrapolated to, the low heating rates. The data for all the polyethylene fractions and for $C_{192}H_{386}$ that will be analyzed here were obtained under these conditions.

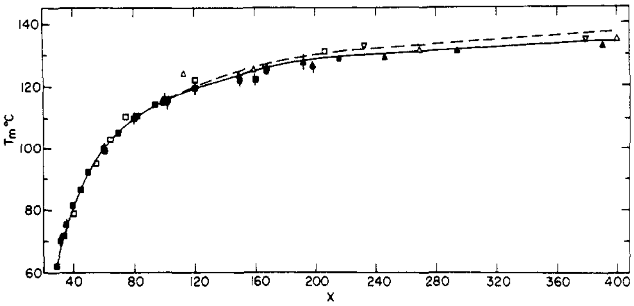

Figure 1. Plot of melting temperature T_m against number of carbon atoms x for n-alkanes (solid symbols) and low molecular weight polyethylene fractions (open symbols). n-Alkanes: (●) ref 5; (▲) ref 7; (●) ref 3; (▲) ref 16; (■) ref 6; (■) ref 23; (▲) ref 39. Polyethylene: (□) ref 13; (△) ref 10; (▽) ref 22.

It is also important to ascertain whether the directly observed melting temperature depends on the crystallization temperature, T_c. For example, even for the n-alkane $C_{192}H_{386}$ an increase of 1.5 °C is found for the equilibrium melting temperature over that directly observed.[16,27] Similar effects are found with the low molecular weight polyethylene fractions that only form extended-chain crystallites.[10,28] For the higher molecular weights ($M_n = 3769$ and 5600) a discontinuity is observed in the T_m–T_c plot.[10] This represents a change from a folded-type crystallite structure to an extended one. Thus, in order to determine the equilibrium melting temperature an analysis must be made of the dependence of T_m on T_c. This procedure was adopted for the polyethylene data analyzed here as well as for $C_{192}H_{386}$. For the reasons cited, therefore, these data can be considered to represent equilibrium melting temperatures. We should note that if the proper sample mass is used, there is a compensating effect in the deviation from equilibrium between the heating rate and the dependence of T_m on T_c.

Among the melting temperature compilations of the high molecular weight n-alkanes, Lee and Wegner[5] studied the range $C_{120}H_{242}$ to $C_{216}H_{434}$ and extrapolated the observed melting temperatures to zero heating rates. However, they did not study the dependence of the observed melting temperature on the crystallization temperature. Thus, their reported melting temperatures would be expected to be ca. 1 °C less than the equilibrium value. Ungar et al.[7] studied the range $C_{102}H_{206}$ to $C_{390}H_{782}$ using the single heating rate of 10 °C/min. They did not examine the dependence of the temperature on the crystallization temperature. It can be presumed that the reported melting points of Bidd et al.[3] for the same compounds described by Ungar et al.[7] followed the same procedure. In these studies a compensation would be expected between the two different effects, and reliable melting temperatures would thus result.[39] Takamizawa et al.[23] studied the melting temperatures of $C_{60}H_{122}$ to $C_{160}H_{322}$ by dilatometry, by differential thermal analysis, and by differential scanning calorimetry. The results obtained by the two different methods complement one another except for $C_{80}H_{162}$, whose melting temperature by DSC appears to be slightly on the low side. A compilation of the reported melting temperatures, determined in the manner described above, is plotted in Figure 1 against x, the number of carbon atoms (number average for the polymer) in the chain. The open symbols represented the data for the polymers, while the closed symbols represented the melting temperatures of the *n*-alkanes. The data plotted in Figure 1 give a most interesting and surprising set of results. We find that with the exception of only one point both chain molecules can be described by a common curve.[29,30] Within 1 °C, all of the melting temperatures fall on the curve described by the solid line in this figure. The agreement is particularly noteworthy with common molecular weights of the two species. Considering the different sources of the data and that both calorimetric and dilatometric techniques were used in different experiments, this leads one to accept the reality of the agreement that is obtained. We then have to seek the reason for the concordance in the melting temperature–molecular weight relations between the *n*-alkanes and the low molecular weight polyethylene fractions.

For polymers, molecular crystals, where the ends from one chain to another are paired and thus delineate well-defined planes, cannot form. No matter how well fractionated the system is, the individual molecules will not be of exactly the same length. Therefore, the necessary condition for molecular crystal formation cannot be physically fulfilled. Consequently, the equilibrium condition, established by statistical mechanical anaylsis,[31] is one where the end portion of the molecule is disordered, or unpeeled. Thus a chain of x repeating units is characterized by an equilibrium crystallite, or ordered sequence length, ζ_e.[31] This model receives verification from several different experimental sources. Solid-state ^{13}C NMR studies at ambient temperature of a low molecular weight linear polyethylene, $M_n = 1600$, show that a higher proportion of α and methyl carbons are in the noncrystalline phase relative to the crystallinity level of the inner methylene carbons.[32] Recent Raman studies[33] with fractions $M_n = 800$ and $M_n = 1000$ indicate that ca. 10–15% of the chain units are disordered and that the disordering process proceeds from the chain ends. These results thus support the theoretically expected equilibrium crystallite structure. Complete melting of the polymers therefore occurs from a partially disordered state.

In contrast to the polymers the primary characteristic of an *n*-alkane is the fact that all of the constituent chain molecules are of precisely the same length and are terminated at each end by a methyl group. Consequently, at sufficiently low temperatures molecular crystals are formed. However, it has been found by several different experimental techniques that if the *n*-alkane is sufficiently long, the molecular crystal structure is not maintained at elevated temperatures. In this case, premelting, with end disordering, takes place prior to complete melting. Calorimetric studies of the fusion process of dononacontahectane, $C_{192}H_{386}$, has demonstrated that this type of premelting takes place ca. 30 °C below the actual melting temperature.[16] The same interpretation can be given to a similar calorimetric study of *n*-hectane, $C_{100}H_{202}$.[16,34] A solid-state ^{13}C NMR study of octahexacontahectane, $C_{168}H_{338}$, in extended crystalline form has shown that significant conformational disorder of the CH_3 groups and the adjacent α and β carbons takes place at 87 °C, which is ca. 40 °C below the true melting temperature.[32] This observation is indicative of premelting and is very similar to the results found for low molecular weight polyethylene at ambient temperature. Other evidence for premelting of this type is found in the dilatometric study of $C_{94}H_{190}$[35] and in the small-angle X-ray studies of $C_{80}H_{162}$ and $C_{94}H_{190}$.[23a,36] Recent infrared and Raman studies of $C_{50}H_{102}$ and $C_{60}H_{122}$ indicate that premelting takes place ca. 30–40 °C below the true melting temperatures of these compounds.[37] A straightforward theoretical explanation of this type of premelting has been given.[6,16] It has been shown that depending on the relative values of the interfacial free energies involved, melting should occur in the pure *n*-alkanes of modest chain lengths. The interfacial free energies that are deduced[10] (cf. seq.) for the junction of the ordered and disordered sequences will satisfy the premelting condition. The premelting phenomenon of interest here is very specific to chain molecules. It is not of the conventional type that is encountered for all classes of molecules that can be attributed by straightforward thermodynamic arguments to the presence of impurities.

We have thus established, on both a theoretical and experimental basis, that the polyethylene fractions and the monodisperse *n*-alkanes display premelting prior to complete melting. At elevated temperatures both systems thus have the same structure, a core crystalline portion and a sequence of disordered end units. These structural factors should be the same for a given molecular weight of either species. Therefore, it should be expected that the same equilibrium melting temperature–molecular weight relation is found for both types of chain molecules.

It is of interest now to examine the quantitative basis for the common melting temperatures of both types of chain molecules. Flory and Vrij have developed a well-founded theory for the melting of end-paired molecular crystals.[6] They pointed out that although the enthalpy of fusion can be taken as a linear function of chain length, the corresponding linearity of the entropy of fusion is not valid. Taking this factor into account along with the temperature dependence of the free energy of fusion and the interfacial free energy associated with the planes of end-paired units, the melting temperature–molecular weight relation was derived for this model. This theoretical relation was applied to the melting temperatures of the *n*-alkanes. The *n*-alkane $C_{100}H_{102}$ was the highest molecular weight then available. The tacit assumption was made in this analysis that premelting did not occur, so that the observed melting temperatures were assumed to reflect the disappearance of the end-paired molecular crystals. On this basis, an equilibrium melting temperature, $T_m{}^\circ = 145.5 \pm 1$ °C, was extrapolated for the infinite molecular weight polyethylene. The melting temperatures that are calculated from this theory for the chain lengths of interest here are represented by the dashed line in Figure 1. Starting with carbon number 120, the theoretical melting temperatures for the molecular crystals are slightly higher than those actually observed. The melting temperatures calculated from the Flory–Vrij theory crucially depend on the assumption that the melting temperatures reported in the range $C_{50}H_{102}$ to $C_{100}H_{202}$ actually represent the melting of molecular crystals. From our previous discussion, we know now that this is not a valid assumption. The Flory–Vrij analysis has been reexamined by restricting the data base of the *n*-alkanes to carbon numbers less than 50.[12] In this chain length range, the effect of end disordering should be minimal, but cannot be completely ruled out. By restricting the data base in this manner, it was found that a much wider range of $T_m{}^\circ$ values, as well as melting temperatures in the region of interest, become compatible with theory.[16] However, despite this finding, it must be recognized that the Flory–Vrij molecular crystal theory cannot be applied to the *n*-alkanes in the range of current interest.

Flory has also calculated the equilibrium melting temperature–molecular weight relation for equilibrium crystallites with disordered end sequences.[31] The melting temperatures can be expressed as

$$1/T_{me} - 1/T_m{}^\circ = (R/\Delta H_u)\{(1/x) + [1/(x - \zeta_e + 1)]\} \quad (1)$$

Table I
Parameters Involved in the Fusion of Low Molecular Weight Polyethylene Fractions

		$T_m°$ = 145.5 °C			$T_m°$ = 144 °C			
M_n	$T_{me}°$, °C	ζ_e	ζ_e/x	σ_e	ζ_e	ζ_e/x	σ_e	ref
575	79	37	0.90	1853	37	0.90	1773	13
785	95	50	0.89	1852	50	0.89	1790	13
910	103	57	0.88	1628	57	0.88	1679	13
1055	110.5	65	0.87	1521	65	0.87	1496	13
1586	124.5	95	0.84	1298	74	0.83	1140	10
1675	122	106	0.87	1785	104	0.86	1581	13
2221	126	140	0.88	2024	139	0.87	1790	10
2900	131	181	0.87	1876	178	0.86	1597	13
3265	133	202	0.87	1746	198	0.85	1462	22
3769	132	242	0.90	2558	238	0.88	2142	10
5320	135	345	0.91	2930	338	0.89	2329	22
5600	134.2	368	0.92	3485	362	0.91	2858	22

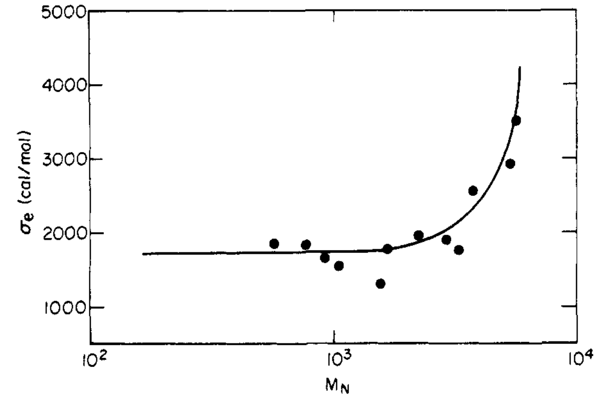

Figure 2. Plot of σ_e (cal/mol) against M_n for linear polyethylene fractions.

$$2\sigma_e = RT_{me}\{[\zeta_e/(x-\zeta_e+1)] + \ln[(x-\zeta_e+1)/x]\} \quad (2)$$

Here, $T_m°$ is the equilibrium melting temperature for an infinite molecular weight chain and T_{me} is the corresponding temperature for a fraction containing x repeating units. σ_e can be taken to be the effective interfacial free energy associated with the basal plane of an equilibrium crystallite of length ζ_e, and ΔH_u is the enthalpy of fusion per repeating unit and has been found to be 980 cal/mol of repeating units. Since extended-chain crystallites are formed by the low molecular weight fractions studied here, these equations should be applicable. Consequently, we have listed in Table I the key parameters that can be deduced from eqs 1 and 2, taking $T_m°$ to be 145.5 and 144.0 °C, respectively. We find from this analysis that although ζ_e increases monotonically with x, as would be expected, the ζ_e/x ratio is of the order of 0.90 for $T_m°$ either 145.5 or 144.0 °C. Extended-chain crystallites of higher molecular weights have not as yet been produced to establish whether a constant, asymptotic value of ζ_e/x can be reached. The answer to the question is directly related to the dependence of σ_e on molecular weight. A plot of σ_e as a function of molecular weight is given in Figure 2. Here, $T_m°$ is taken as 145.5 °C, but very similar results are obtained for other selected equilibrium melting temperatures in this vicinity. In the low molecular weight range, $M_n \leq 2000$, a fairly constant value of ca. 1700 cal/mol is found for σ_e. However, for $M_n \geq 2000$, there is a definite increase in the observed value of σ_e, which reaches a value of 3000–3500 cal/mol for M_n = 5600. It has been pointed out previously in detail that the increase in σ_e with molecular weight is caused by the first term on the right in eq 2.[10,40] Although the interfacial free energy would be expected to reach an asymptotic value with chain length, it clearly has not done so for the highest molecular weights studied up till now where extended-chain crystallites are formed.

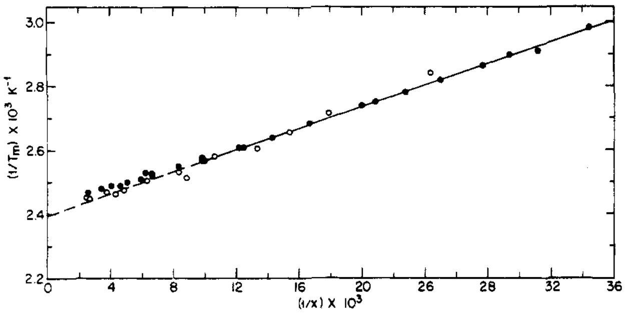

Figure 3. Plot of $1/T_m$ against $1/x$ for n-alkanes (●) and low molecular weight polyethylene fractions (○).

This variation in σ_e with molecular weight makes it difficult using these data, as well as those of the n-alkanes, to extrapolate to $T_m°$ characteristic of the infinite molecular weight chain. This problem can be seen in the following analysis. Equation 1 can be rewritten as[31]

$$1/T_{me} - 1/T_m° = (R/\Delta H_u)(1+b)(1/x) \quad (3)$$

where $b = [1 - (\zeta_e/x) + (1/x)]^{-1}$. The quantity b then depends on σ_e through the ratio ζ_e/x. If b were a constant, then a plot of $1/T_{me}$ against $1/x$ should be linear and extrapolate to $1/T_m°$ as $x \to \infty$. Although we recognize that ζ_e/x (or σ_e) has not reached an asymptotic value, so that b is not a constant for the data currently available, it is instructive to analyze these data in terms of the above. Consequently, the appropriate plot is made in Figure 3 for the available polymer and n-alkane data. Careful scrutiny of this plot indicates that the data points are not sufficiently linear to yield a reliable extrapolation for $T_m°$. Drawn solely as basis for reference, the straight line given in Figure 3 yields a value of $T_m°$ = 144.3 °C. It is clear that in order to accomplish a reliable extrapolation for $T_m°$ from this type analysis, melting temperatures for both polymer and the n-alkane in the region $1/x = 1 \times 10^{-3}$ to 2×10^{-3} are required. Thus at this point, one cannot offer a more precise value for $T_m°$. Estimates of the asymptotic value of σ_e indicate that $T_m°$ can be within 1 °C of the value indicated.

In summary, we conclude that the extrapolation to $T_m°$ of the melting temperatures of the n-alkanes and the low molecular weight polyethylene fractions cannot be accomplished with reliability at the present time. Although the Flory–Vrij theory for the chain length dependence of the melting temperature of the n-alkanes is on theoretically firm basis, it cannot be applied to this problem because of premelting. The premelting in the n-alkanes involves disordering of the end sequences and is the reason for the identical melting temperatures of the polymers and n-alkanes. As has been pointed out, the extrapolation to infinite chain length of the equilibrium melting temperatures of the finite chain systems is severely hampered because of the molecular weight dependence of σ_e.

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References and Notes

(1) Paynter, O. I.; Simmonds, D. J.; Whiting, M. C. *J. Chem. Soc., Chem. Commun.* **1982**, 1165.
(2) Bidd, I.; Whiting, M. C. *J. Chem. Soc., Chem. Commun.* **1985**, 543.
(3) Bidd, I.; Holdup, D. W.; Whiting, M. C. *J. Chem. Soc., Perkin Trans 1* **1987**, 2455.
(4) Lee, K. S. Thesis, Freiburg, FRG, 1984.
(5) Lee, K. S.; Wegner, G. *Makromol. Chem., Rapid Commun.* **1985**, *6*, 203.
(6) Flory, P. J.; Vrij, A. *J. Am. Chem. Soc.* **1963**, *85*, 3548.
(7) Ungar, G.; Stejny, J.; Keller, A.; Bidd, I.; Whiting, M. C. *Science (Washington, D.C.)* **1985**, *229*, 386.
(8) Kloos, F.; Go, S.; Mandelkern, L. *J. Polym. Sci., Polym. Phys. Ed.* **1974**, *12*, 1145.
(9) Leung, W. M.; Manley, R. St. J.; Panaras, A. R. *Macromolecules* **1985**, *18*, 760.
(10) Stack, G. M.; Mandelkern, L.; Voigt-Martin, I. G. *Macromolecules* **1984**, *17*, 321.
(11) Kloos, F.; Go, S.; Mandelkern, L., unpublished results.
(12) Stack, G. M.; Mandelkern, L. *Macromolecules* **1988**, *21*, 510.
(13) Prasad, A.; Mandelkern, L. *Macromolecules* **1989**, *22*, 914.
(14) The concept of a folded-chain crystallite is used only in the context that the crystallite thickness is not comparable to the extended chain length. This phraseology carries no implications as to the interfacial structure of the basal plane of the lamella crystallite.
(15) Hoffman, J. D. *Polym. Commun.* **1986**, *27*, 39.
(16) Stack, G. M.; Mandelkern, L.; Kröhnke, C.; Wegner, G. *Macromolecules*, **1989**, *22*, 4351.
(17) Ungar, G.; Keller, A. *Polymer* **1986**, *27*, 1835.
(18) Ungar, G.; Organ, S. J. *Polym. Commun.* **1987**, *28*, 232.
(19) Organ, S. J.; Keller, A. *J. Polym. Sci., Polym. Phys. Ed.* **1987**, *25*, 2409.
(20) Ungar, G.; Keller, A. *Polymer* **1987**, *28*, 1899.
(21) Organ, S. J.; Ungar, G.; Keller, A. *Macromolecules* **1989**, *22*, 1995.
(22) Fatou, J. G.; Mandelkern, L. *J. Phys. Chem.* **1965**, *69*, 417.
(23) Takamizawa, K.; Sasaki, Y.; Kono, K.; Urabe, Y. *Rep. Prog. Polym. Phys. Jpn.* **1976**, *19*, 285. Takamizawa, K.; Ogawa, Y.; Oyama, T. *Polym. J.* **1982**, *14*, 441.
(24) Broadhurst, M. G. *J. Res. Natl. Bur. Stand.* **1962**, *66A*, 241.
(25) Mandelkern, L.; Stack, G. M.; Mathieu, P. J. *Anal. Calor.* **1984**, *5*, 223.
(26) Alamo, R.; Mandelkern, L. *J. Polym. Sci., Polym. Phys. Ed.* **1986**, *24*, 2087.
(27) Recent studies with the *n*-alkane $C_{168}H_{338}$ show a very similar effect.[39]
(28) Prasad, A.; Mandelkern, L., unpublished results.
(29) The one exception has been previously noted[10] and can probably be attributed to a small error in the molecular weight determination.
(30) In this compilation, the results of experiments where the lamellar crystallites were etched (degraded with fuming nitric acid) are not included.[38] The purity of the resulting samples and the significance of the molecular weight and melting temperature determination suggest caution in including these data.
(31) Flory, P. J. *J. Chem. Phys.* **1949**, *17*, 223.
(32) Möller, M.; Cantow, H.; Drotloff, J.; Emeis, D.; Lee, K. S.; Wegner, G. *Makromol. Chem.* **1986**, *187*, 1237.
(33) Snyder, R. G., private communication.
(34) Hay, H. N. *J. Polym. Sci., Polym. Lett.* **1970**, *8*, 395.
(35) Mandelkern, L. Crystallization and Melting of Polymers. In *Comprehensive Polymer Science, Vol. 2, Polymer Properties*; Booth, C., Price, C., Eds.; Pergamon Press: New York, 1989.
(36) Sullivan, P. K.; Weeks, J. J. *J. Res. Natl. Bur. Stand.* **1970**, *74A*, 203.
(37) Kim, Y.; Strauss, H. L.; Snyder, R. G. *J. Phys. Chem.*, in press.
(38) Wunderlich, B.; Czornyj, G. *Macromolecules* **1977**, *10*, 906.
(39) Stack, G. M.; Mandelkern, L., unpublished observation.
(40) Mandelkern, L.; Stack, G. M. *Macromolecules* **1984**, *17*, 871.

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Time–Cure Superposition during Cross-Linking†

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ABSTRACT: Using a dynamic scaling theory for the viscoelasticity of cross-linking polymers near the gel point, we predict the superposition of viscoelastic functions at differing extents of reactions. For example, to superpose the stress relaxation modulus, a vertical shift is needed to account for the increase in the equilibrium modulus with cure, $G_\infty \sim \epsilon^{8/3}$, and a horizontal shift for the divergence of the characteristic relaxation time, $\tau_z \sim \epsilon^{-4}$, where ϵ is the critical extent of reaction. Experiments on model epoxies show excellent superposition both below and above the gel point and give $G_\infty \sim \epsilon^{2.8\pm0.2}$ and $\tau_z \sim \epsilon^{-3.9\pm0.2}$. The critical regime where this superposition is valid is surprisingly wide, encompassing over half of the reaction.

Introduction

Although the critical dynamics that occur near a *thermodynamic* second-order phase transition are reasonably well understood, the critical dynamics of the gel point, a second-order transition in *connectivity*, have been investigated only recently.[1–5] At the sol–gel transition it is the divergent connectivity correlation length, not the spatial correlation length, that leads to complex dynamic behavior, so there are many interesting viscoelastic dynamical features that have no apparent analogue in thermodynamic transitions. The observed phenomenology is by now familiar: beneath the gel point, the viscosity η diverges continuously and above the gel point the equilibrium modulus G_∞ grows continuously. In addition, the longest relaxation time,[6] τ_z, that delineates the simple viscous or elastic regime from a complex viscoelastic fluid regime diverges as the gel point is approached from either

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