# Notes

## Melting Temperature of Mixed-Microstructure Polybutadiene

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Polymerization of butadiene with lithium alkyls in hydrocarbon media produces a chemical microstructure with roughly equal amounts of 1,-cis and 1,4-trans units and a lesser amount (~8%) of 1,2 (vinyl) units.[2] The high molecular weight versions of those polymers appear to be amorphous at all temperatures. For example, no calorimetric evidence has been reported for a phase transition from the glass temperature, $T_g \sim -99$ °C, to temperatures in excess of 100 °C. This absence of crystallinity seems reasonable in view of the mixed microstructure and similar results for other copolymer-like systems such as stereoirregular polystyrene. The purpose of this note is to report some observations on low molecular weight polybutadienes with this microstructure which suggest the occurrence of crystallization at low temperatures.

### Experiments

In the course of measuring viscoelastic properties for a series of polybutadienes (polymerized by *sec*-butyllithium in cyclohexane, with resulting polydispersity $\bar{M}_w/\bar{M}_n < 1.1$[3]), we noticed the development of time-dependent anomalies in the response of several low molecular weight samples ($M < 2.5 \times 10^3$) at low temperatures. Above −20 °C the linear response was typical for polymer liquids.[4] The dynamic modulus $G^*(\omega)$ was independent of holding time at each temperature, and data for different temperatures could be superimposed by shifts in the frequency scale with minor adjustments in the modulus scale. At −50 °C the response depended on holding time; $G^*(\omega)$ increased progressively with time, with the largest changes occurring at lower frequencies. For higher molecular weight samples with very similar cis/trans/vinyl ratios ($M \geq 80 \times 10^3$), the behavior was conventional and typical of polymer liquids over the full range of test temperatures, $-75 < T < +150$ °C.

To clarify these observations, four samples of low molecular weight polybutadiene were investigated by differential scanning calorimetry (Perkin-Elmer DSC-2). Molecular weights and microstructures are given in Table I (samples A–D). Characterization data for two polymers of higher molecular weight but similar microstructure (samples E and F) are also included. In addition to microstructure determinations by FTIR and $^1$H NMR, we selected low and high molecular weight examples, samples B and E, for 1,4-diad measurement by 75-MHz $^{13}$C NMR.[5] The diads were calculated from the four resolvable olefinic carbon resonances. Solutions in deuterated chloroform were used with Cr(acac)$_3$ added to decrease $T_1$. These data are given in Table II.

To correspond in a rough way with the viscoelastic observation ranges, the following DSC thermal history was used for all samples. The temperature was first lowered to −53 °C (220 K) and held for 30 min. The temperature was then lowered to −93 °C and scanned from −93 to −13 °C at 20 °C/min. A broad endotherm between −50 and −25 °C was observed for each polymer, as shown in Figure 1. The magnitude of this endotherm decreases with increasing molecular weight until it is barely discernible above the noise for sample D ($M = 41 \times 10^3$). Endotherm areas were converted to enthalpy/mass; the values obtained are given in Table III.

**Table I**
**Molecular Characterization Data**

| sample | $M \times 10^{-3}$ | DP | % 1,4-cis[a] | % 1,4-trans[a] | % 1,2[a] |
|---|---|---|---|---|---|
| A | 1.1 | 21 | 34 | 58 | 8 |
| B | 3.9 | 73 | 35 | 57 | 8 |
| C | $10_{.5}$ | 194 | 35 | 56 | 9 |
| D | 41 | 760 | 36 | 56 | 8 |
| E[b] | 79 | 1460 | 37 | 54 | 9 |
| F | 81 | 1500 | 39 | 53 | 8 |

[a] Obtained by Fourier transform infrared measurements. Values of cis/trans/vinyl were also determined by proton nuclear magnetic resonance measurements on selected samples: 38/54/8 and 40/51/9 were obtained for samples D and E by $^1$H NMR, and 41/51/8 and 42/50/8 for samples B and E by $^{13}$C NMR. [b] Sample E was prepared in 9/1 cyclohexane–benzene solution at 25 °C by vacuum line techniques. The remaining samples were prepared in cyclohexane at 50 °C in a nitrogen atmosphere.

**Table II**
**1,4-Diad Fractions[a]**

| sample | trans,cis | trans,trans | cis,cis | cis,trans |
|---|---|---|---|---|
| B | 0.27 (0.25) | 0.29 (0.31) | 0.19 (0.19) | 0.25 (0.25) |
| E | 0.27 (0.25) | 0.27 (0.29) | 0.22 (0.21) | 0.23 (0.25) |

[a] Experimental values, obtained from 75-MHz $^{13}$C NMR spectra.[5] Values in parentheses were calculated from the overall cis and trans contents by using Bernoullian statistics.

**Table III**
**Calorimetric Results**

| sample | melting range, °C | melting enthalpy, cal/g | % crystallinity |
|---|---|---|---|
| A | −49 to −27 | $1.0_4$ | 5.6 |
| B | −51 to −24 | 0.73 | 3.9 |
| C | −51 to −25 | 0.25 | 1.3 |
| D | −49 to −25 | ~0.09 | ~0.5 |

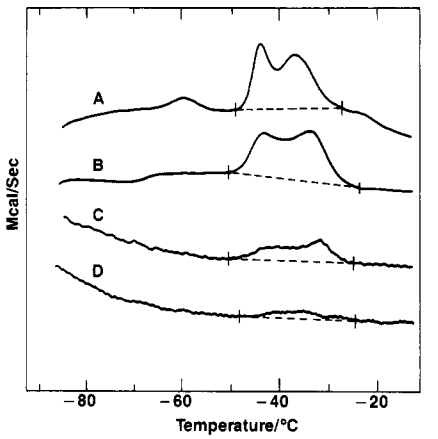


**Figure 1.** DSC melting curves for samples A–D. Sample size was 10–15 mg; scan rate was 20 °C/min. Vertical marks indicate the visually chosen beginning and end of each endotherm; the dashed line indicates the assumed base line of each endotherm for the calculation of melting enthalpy (Table II).

The endotherms appear to reflect crystallization of some portion of the enchained units during the 30-min holding period at −53 °C. It seems reasonable that the crystallizing species are parts of 1,4-trans sequences in the polymer since the trans isomer is the major component, and the melting temperature of the trans "homopolymer" is fairly high ($T_m = 97$ °C for one crystalline form and 145 °C for the other[6]). We have used the reported enthalpy

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of melting of the lower melting form, 1.0 kcal/mol of $C_4H_6$ units,[6] to recast the melting enthalpy of our samples as a nominal percent crystallinity (Table III).

## Discussion of Results

The final melting temperature $T_m$ is practically independent of molecular weight. We assume that the value obtained, $T_m = -26 \pm 1$ °C, is thermodynamic in origin and that it depends primarily on the concentration of trans sequences which exceed some critical length. Judged by the constancy in overall composition of the samples (Table I) and the virtually identical diad content of low and high molecular weight samples (Table II), the sequence distribution probably does not change very much with molecular weight. It is mildly surprising, however, to find such a weak molecular weight effect on $T_m$ even for sample A in which the number of monomer units per chain (DP) is only 21; perhaps the very slight trend in trans content offsets the chain-end effect. Melting transitions have been observed dilatometrically for polybutadienes from free radical polymerization.[7,8] The values of $T_m$ reported—37, 23, and 0 °C at 81%, 73%, and 64% 1,4-trans contents—extrapolate to values that are in reasonable accord with our result of $T_m = -26$ °C at 57% trans.

The amount of crystallinity obtained during the 30-min interval at −53 °C decreases rapidly with increasing molecular weight. We assume this behavior is primarily kinetic in origin, although equilibrium effects associated with the chain length certainly cannot be ruled out. Crystallizable sequences in the longer chains are likely to be less mobile, so it is not unexpected to find that the extent of crystallization decreases with increasing molecular weight for a fixed supercooling and incubation period. For the thermal history employed here, the calorimetric evidence for crystallinity disappears into the noise beyond $M = 40 \times 10^3$.

Low-frequency viscoelastic measurements should be extremely sensitive to traces of crystallinity, especially for long chains where even minute amounts would convert the liquid to a network. Crystallization is almost certainly the cause of our problems with viscoelastic measurements below −25 °C for the low molecular weight samples. No such effects were encountered in viscoelastic measurements on samples of similar microstructure but higher molecular weight (samples E and F, Table I). Conventional polymer liquid behavior was observed down to −75 °C for those samples, even with typical holding times (for purposes of temperature equilibration and data acquisition) of several hours between −75 and −25 °C.

## Conclusions

We have shown that the final melting temperature $T_m$ for the typical representatives of mixed-microstructure polybutadiene examined here is near −26 °C and that $T_m$ for microstructures in this range is insensitive to chain length. Even well below −26 °C the degree of crystallinity is vanishingly small for modest holding times (on the order of hours) when the molecular weight exceeds $M = 50 \times 10^3$.

These observations are relevant to a recent discussion about crystallinity in mixed-microstructure polybutadienes[9] and the possible influence of crystallization on the mechanical properties of polybutadiene networks at 25 °C.[10] It now seems clear that the theoretical estimates of $T_m$ for mixed-microstructure polybutadienes presented there[9] are much too high. This is not surprising since, for example, the contribution of crystallite surface energies was not considered, and that contribution is usually rather large in copolymers.[11] Estimates of $T_m$ ranging from 30 to 60 °C were given for mixed-microstructure polybutadienes of the sort examined here,[9] it seems from our work that the true value for such polymers must lie well below 0 °C. This judgment is supported by calorimetry on Phillips Trans-4 polybutadiene (93% trans units). For that polymer we obtained $T_m \sim 57$ °C (at scan rates of 1.25 and 5 °C/min) and ~60% crystallinity. According to the theoretically estimated behavior presented in Figure 1 of ref 9, $T_m$ of Trans-4 should have been nearly 90 °C. In view of the results presented here, the large values of initial (small strain) modulus at 25 °C in mixed-microstructure polybutadiene networks relative to classical network predictions[10] cannot reasonably be attributed to crystallinity.

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**Registry No.** polybutadiene, 9003-17-2.

## References and Notes

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# Polymerization and Characterization of Liquid Crystalline Poly(hexyl isocyanate)/Styrene Solutions

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In recent years, interest in preparing molecular composites composed of rigid-rod and random coil polymers has escalated owing to the potential these unique polymer blends have for exhibiting combinations of desirable features, including high strength, toughness, and processibility. In general, it has been difficult to prepare homogeneous blends of high molecular weight polymers. This has been particularly true for polymers possessing significantly different conformations. Several approaches have been developed recently, however, which are relatively

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