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Effect of Long Branches on the Temperature Dependence of Viscoelastic Properties in Polymer Melts

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ABSTRACT: In some polymer species the presence of long branches leads to an increase in the temperature coefficient of melt viscosity and departures from time–temperature superposition. In other species the temperature dependence is apparently unchanged by branching. We suggest here two possible explanations for these remarkable and species-dependent properties. One has to do with the temperature dependence of the entanglement density, and the other with the unusual compactness of conformations in the transition state for relaxation of long branches, as suggested by recent theories. Data on model polyethylenes suggest that both mechanisms may be important. In either case the temperature effects should depend on the energy difference of trans and gauche conformers, a property that also governs the temperature coefficient of chain dimensions, $\kappa = \mathrm{d}\ln\langle r^2\rangle/\mathrm{d}T$, for the species. Literature values of κ for the species that have been studied so far are consistent with observations.

The flow properties of linear and branched polymers differ substantially in the entanglement regime. When the branches are long compared to the entanglement spacing, the relaxation spectrum is broadened, and the slowest relaxations are shifted to much longer times.[1,2] As a result, the zero-shear viscosity η_0 and the steady-state recoverable compliance J_e^0 depend on polymer molecular weight M and volume fraction ϕ differently for linear and branched polymers. Empirically, for f-arm stars with narrow molecular weight distribution[1]

$$(\eta_0(M))_B \sim (\eta_0(gM))_L \exp[\gamma(M_b/M_e)] \tag{1}$$

$$(J_e^0)_B \sim \frac{2}{5}g_2\frac{M}{\phi\rho RT} \tag{2}$$

in which

$$g = (3f-2)/f^2 \tag{3}$$

$$g_2 = (15f-14)/(3f-2)^2 \tag{4}$$

and where ρ is the undiluted polymer density, f is the branched point functionality ($M_b = M/f$), γ is a constant for stars of the same functionality, $(\eta_0)_L$ is the viscosity of linear chains with the same radius of gyration as the stars ($(\eta_0)_L \propto (gM)^{3.4}$), M_e is the entanglement molecular weight

$$M_e = \rho\phi RT/G_N^0 \tag{5}$$

and G_N^0 is the plateau modulus ($G_N^0 \propto \phi^a$, a = 2–2.3 (ref 3)). Thus, when the branches are highly entangled ($M_b/M_e \gg 1$), the viscosity increases exponentially with arm length.[4] The recoverable compliance varies as $\phi^{-1}M^1$ in contrast with $J_e^0 \sim 2.5(G_N^0)^{-1} \propto \phi^{-a}M^0$ for linear chains.[5]

Recent work at this laboratory has shown that long branches can also cause substantial changes in the temperature dependence of viscoelastic properties.[6] The most extensive studies have been made with linear and star-branched models for polyethylene, prepared by hydrogenation of polybutadienes (~92% 1,4) with narrow molecular weight distributions. The linear and star products have narrow distributions and the same chemical microstructure, equivalent to that of random copolymer of ethylene with ~4 mol % 1-butene. The linear samples are practically indistinguishable from linear polyethylene fractions in the melt state. Melt viscosities at 190 °C are the same within experimental error. The flow activation energy E_a

$$\eta_0(T) \propto \exp(E_a/RT) \tag{6}$$

is independent of chain length, and it differs only slightly between linear polyethylene (E_a = 6.4 kcal) and the hydrogenated polybutadienes (E_a = 7.1 kcal). The dynamic moduli, $G'(\omega)$ and $G''(\omega)$, obey the time–temperature superposition principle.

The stars, however, are thermorheologically complex: the shapes of the modulus–frequency curves change with temperature.[6] Compared to linear chain behavior the slowest relaxations shift more rapidly with temperature. The shift factor decreased progressively with increasing frequency and eventually levels off at the value for linear chains. The effect increases with branched length. For example, the flow activation energy for viscosity (dominated by the slow relaxations) reaches ~15 kcal for $M_b \sim 30\,000$ in the 3-arm stars. Such behavior is not confined to star polymers. Randomly branched commercial polyethylenes have increased flow activation energies[7] and are also thermorheologically complex.[8]

Subsequent work has shown that the difference due to branching, $\Delta E = (E_a)_B - (E_a)_L$, decreases smoothly to zero as the branch length decreases and also as the branched polymer is diluted with low molecular weight hydrocarbons.[6] It appears in fact that ΔE is directly proportional to M_b/M_e, and thus ΔE varies in the same way as the exponent in eq 1, i.e., as the number of chain entanglements along the branch. Similar differences are observed between linear and star versions of hydrogenated polyisoprene (~92% 1,4)[9] and polybutadiene of much higher vinyl content (~65% 1,4),[10] materials with the microstructures of ethylene–propylene and ethylene–1-butene copolymers, which are amorphous at all temperatures. Thus, *the effect is not peculiar to polyethylene melts alone*, and it is not associated with "crystallizability", as suggested earlier.[6]

These observations are puzzling for several reasons. First, time–temperature superposition is an extremely general and experimentally well-established principle in homogeneous polymer melts.[11] To find departures of such magnitude in simple hydrocarbon polymers is therefore quite surprising. Second, for long chains the temperature shift factor normally depends only on the chemical microstructure.[11] In this case, however, the effect becomes larger as the concentration of long-chain branch points in the system decreases, i.e., as the branches become longer. Third, the effect depends on polymer species. Stars of polystyrene,[12] polybutadiene,[2] and polyisoprene[9] behave conventionally. The spectrum is broadened and the viscosity is enhanced by long branches, but time–temperature superposition is apparently obeyed, and differences in temperature coefficient from their linear homologues are negligible. How can such seemingly anomalous charac-

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teristics of only certain species be explained?

There is one possibility, based on the temperature dependence of chain dimensions, that can be tested rather directly. According to eq 1, the temperature dependences of linear and star polymers would differ if the exponential term

$$\Gamma = \exp[\gamma(M_b/M_e)] \tag{7}$$

varied with temperature. From eq 5 the exponent is $\gamma M_b G_N{}^0/\phi\rho RT$. It has been proposed recently that $G_N{}^0$ varies with temperature as[3]

$$\frac{G_N{}^0(T_2)}{G_N{}^0(T_1)} = \frac{\rho^2(T_2)T_2C_\infty(T_2)}{\rho^2(T_1)T_1C_\infty(T_1)} \tag{8}$$

where $C_\infty(T)$ is the characteristic ratio of the species at temperature T.[13] Thus, assuming γ is independent of temperature,

$$\frac{\Gamma(T_2)}{\Gamma(T_1)} = \exp\left[\frac{\gamma M_b}{M_e(T_1)}\left(\frac{\rho(T_2)C_\infty(T_2)}{\rho(T_1)C_\infty(T_1)} - 1\right)\right] \tag{9}$$

or

$$\ln\frac{\Gamma(T_2)}{\Gamma(T_1)} = \left(\frac{(\rho C_\infty)_{T_2}}{(\rho C_\infty)_{T_1}} - 1\right)\ln\Gamma(T_1) \tag{10}$$

The density $\rho(T)$ is a decreasing function of temperature, and the $C_\infty(T)$ may increase or decrease with temperature, depending on the species. For polyethylene C_∞ decreases about 7% from 130 to 190 °C (based on $\mathrm{d}\ln C_\infty/\mathrm{d}T = 1.15 \times 10^{-3}$ °C^{-1} from thermoelastic measurements[13]), and ρ decreases by about 4%.[14] At $T_1 = 130$ °C for a 3-arm star polyethylene with $M_b = 33\,000$, $\Gamma(T_1) = 223$.[6] With $T_2 = 190$ °C

$$\ln\frac{\Gamma(T_2)}{\Gamma(T_1)} = -0.11 \ln 223 = -0.59$$

When expressed as an apparent flow activation energy, this corresponds to a difference between the linear and branched polymer of $\Delta E = (E_a)_B - (E_a)_L = 3.6$ kcal. Although certainly a significant difference, it still accounts for less than half the observed value,[6] $\Delta E = 14.9 - 7.1 = 7.8$ kcal.

Stress relaxation and the rate of rearrangement of chain conformation are closely related properties in all polymer liquids. Recent theories suggest that the paths for rearrangement of large-scale conformation are different for linear chains and branched chains in entangled systems. That offers an alternative explanation of temperature anomalies, as explained below.

Each chain in an entangled polymer system is surrounded all along its length by neighboring chains. These are assumed to behave like a meshwork of uncrossable lines. The chain can move sideways some distance d, the effective mesh spacing. It can even infiltrate the mesh to some extent by the projection of loops, but its contour can never pass through any of the strands, and sustained sideways motions are suppressed. The mean path of the chain contour through the mesh defines its large-scale conformation. If the chain is linear, it can move to new conformations by reptation,[15,16] i.e., by simple diffusion along its curvilinear path through the mesh (Figure 1). In this case the temperature coefficient of all relaxation times should reflect primarily the temperature coefficient of D^*, the curvilinear diffusion coefficient:

$$(\eta_0)_L \propto (\tau)_L \propto (D^*)^{-1} \tag{11}$$

and thermorheological simplicity is expected.

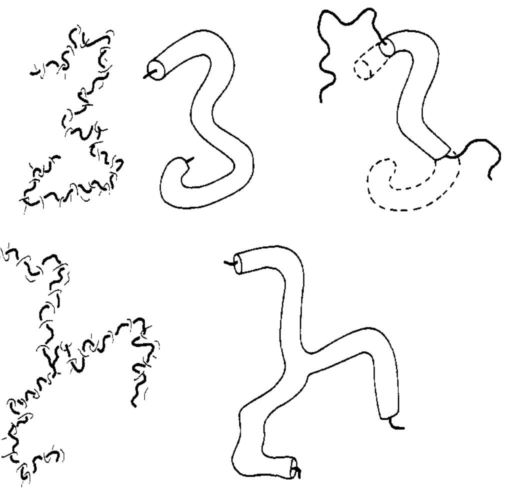

Figure 1. Illustration of the constraining effects of chain-like surroundings for linear molecules and star molecules. A linear molecule can diffuse along its tube of constraints to reach new conformations. Long branches block that motion.

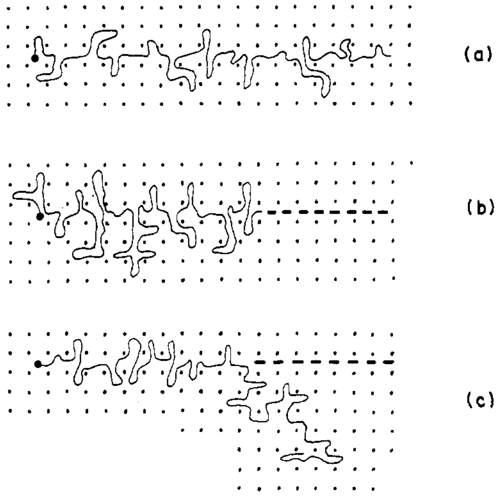

Figure 2. Conformations of a long branch in an entangled system. The initial path (a) is partially abandoned by a temporary increase in the proportion of loops (b). The free end moves out along a random path as the fluctuation subsides (c).

Long branches are assumed to block reptation[17,18] (Figure 1). Rearrangement must then proceed by some other (presumably slower) process. Relaxation times should be longer, which is consistent with the observed enhancement of viscosity by long branches (eq 1).

Each arm of a star molecule can still rearrange its conformation through fluctuations in the length of its path through the mesh.[17,19,20] Infiltration of the mesh by loop projection will vary with time around some average (Figure 2). The free end will move toward the branch point if the total length of loops momentarily increases. It moves away again as that fluctuation subsides, but now along some new path through the mesh. Larger fluctuations must occur in order to rearrangement those parts of the chain path near the branch point, so any initial conformation will "evaporate" more and more slowly from the free end inward. Relaxation by this process of "path breathing" thus requires the branch to pass through a sequence of conformations that are increasingly more compact, i.e., with progressively more reversals in chain direction than the average. The probability of such "highly looped" states decreases exponentially with arm length,[17] consistent with eq 1.

Abnormally compact conformations must certainly contain increased frequencies of gauche states along the backbone and thus fewer trans states. When these conformers have the same energy, the excess free energy of the transition state will be purely entropic; when gauche states have higher energy the chains must pass through states of higher energy as well as lower entropy. Since the time between fluctuations should vary with temperature with $(D^*)^{-1}$,[20] the viscosity should vary like

$$(\eta_0)_B \propto (D^*)^{-1} \exp(\Delta F^\ddagger / RT) \qquad (12)$$

where $\Delta F^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$ is the transition state free energy for the longest relaxation time, and $\Delta H^\ddagger \sim E^\ddagger$ is proportional to the number of gauche conformers along the chain in excess of equilibrium. When $D^* \propto \exp(-E^*/RT)$, the flow activation energies for linear and star versions of the species are

$$(E_a)_L = E^* \qquad (13)$$

$$(E_a)_B = E^* + E^\ddagger \qquad (14)$$

Thus, the temperature coefficients of viscosity for linear and branched polymers can differ owing to the energy difference between gauche and trans conformers, $\Delta\epsilon$. It seems reasonable to assume that the number of excess reversals in the transition state is proportional to M_b/M_e, the average number of entanglements along the branch. In that case, $E^\ddagger$ should be of the form

$$E^\ddagger = K\Delta\epsilon \frac{M_b}{M_e} = K\Delta\epsilon \frac{M_b G_N^0(\phi)}{\rho\phi RT} \qquad (15)$$

and K should be relatively insensitive to temperature, concentration, and polymer species. Accordingly, if $\Delta\epsilon > 0$, the flow activation energy should increase linearly with branch length in melts and also with G_N^0/ϕ in solutions, as observed in the model polyethylenes.[6]

Thermorheological complexity also follows in a natural way. The number of excess loops required to rearrange the conformation of segment k (counting in from the free end of the branch) is proportional to k. Thus, the activation energy associated with the rearrangement of that segment is

$$E_a(k) = E^* + E^\ddagger \frac{k}{n} \qquad (k = 1, 2, ..., n) \qquad (16)$$

where n is the total number of segments in the branch. Accordingly, the temperature coefficients of the fast relaxations (small k) will be practically the same as the linear species, but they will increase progressively ($\Delta\epsilon > 0$) and finally (for $k \sim n$) reach the flow activation energy for the viscosity.

Energy differences among conformers also govern the temperature dependence of unperturbed chain dimensions in the species. If $\langle r^2 \rangle_0$ decreases with increasing temperature, the more compact conformations have higher energy. Thus, there should be a correspondence between $E^\ddagger$ and $\mathrm{d}\langle r^2 \rangle_0/\mathrm{d}T = \mathrm{d}C_\infty/\mathrm{d}T$: long branches should increase the flow activation energy in those species with negative values of $\mathrm{d}C_\infty/\mathrm{d}T$.

Values of $\mathrm{d} \ln \langle r^2 \rangle_0/\mathrm{d}T = \mathrm{d} \ln C_\infty/\mathrm{d}T = \kappa$ are known for many species from thermoelastic measurements.[22] Values can also be estimated from the rotational isomeric model.[13] For polyethylene $\kappa = -1.15 \times 10^{-3}$ °C^{-1}, which is not only negative but also rather large in magnitude compared to most other species. It is also negative for alternating ethylene–propylene copolymers (hydrogenated 1,4-polyisoprene)[23] and roughly comparable in magnitude with κ for polyethylene. No experimental data on κ are available for copolymers of ethylene and 1-butene, but, judged by the calculations for ethylene–propylene copolymers, relatively large negative values are still expected near 30–40% 1-butene compositions. Thus, in those species where E_a is known to increase with branching, the more compact conformations have higher energies.

Judged by data for *cis*-1,4- and *trans*-1,4-polyisoprene,[22] the value of κ for anionic polyisoprene (~70% cis, 20% trans microstructure) is probably quite near zero. Values for *cis*-1,4- and *trans*-1,4-polybutadiene are opposite in sign and roughly equal in magnitude,[22] so it seems likely that κ is quite small for the anionic polybutadienes (~40% cis, 50% trans). The value of κ for anionic polystyrene is somewhat uncertain, but thermoelastic coefficients and measurements in Θ solvents at different temperatures suggest that κ is positive but small in magnitude ($\kappa \sim +0.4 \times 10^{-3}$ °C^{-1} [22]) compared to polyethylene and the ethylene copolymers cited earlier. Thus, those species where long branches have little effect on the temperature coefficient of viscosity also have small temperature coefficients of chain dimensions.

Unfortunately, no viscoelastic data are available on branched polymers for species that have large positive values of κ. For that case one might expect long branches to reduce the temperature coefficient and perhaps even change its sign.

The discussion so far has assumed that the temperature dependence of D^* is governed by an Arrhenius activation energy E^*. That is probably a good approximation for polyethylene, where measurements are available only well above the glass transition temperature, but in general (nearer T_g) one would expect much larger temperature coefficients of the WLF type.[11] Thus,

$$(\eta_0)_L \propto a_T \qquad (17)$$

in which

$$\ln a_T \propto A/(T - T_0) \qquad (18)$$

and A and T_0 depend on the polymer species, diluent, etc. The long-branch effect should remain Arrhenius at all temperatures however, only the probability of compact conformations being involved, so the expectation is

$$(\eta_0)_B \propto a_T \exp(E^\ddagger/RT) \qquad (19)$$

Differences in temperature coefficient due to long branches will thus become increasingly difficult to detect as the temperature is lowered toward T_g since $-(\mathrm{d} \ln a_T/\mathrm{d}T)$ becomes very large. The relatively large temperature coefficient of linear polystyrene may in fact have masked any differences due to branching in that polymer. The effects will be most obvious, of course, for species with small temperature coefficients for linear chains, but then only when M_b/M_e is quite large.

It is useful to consider some of the magnitudes involved. In polyethylene $\Delta\epsilon$ is 600–1000 cal,[24] and M_e is about 1300.[5] For a 3-arm star model polyethylene with $M_b = 33\,000$ the flow activation energy E_a is 14.9 kcal, higher by 7.8 kcal than that for linear chains with the same microstructure. This corresponds to an excess of 8–13 gauche conformers along the branch, or 0.3–0.5 per entanglement. Thus, only relatively small alterations in the distribution of local conformations would be required to account for the entire effect.

Summary

Two possible explanations for differences in the viscoelastic temperature coefficients of linear and branched polymer liquids have been proposed. Both are related to the temperature coefficient of chain dimensions and only operate when the branches are long enough to be extensively entangled. One is based on variations in the entanglement spacing with temperature, which changes the exponential viscosity enhancement factor. From data for

model polyethylenes this contribution is significant but probably too small to account for all of the observed behavior. The other is based on differences in the paths for conformational relaxation of linear and branched chains, as suggested in recent theories. Linear chains rearrange by reptation; long branches rearrange by passing through relatively compact conformational states that may have different energies, depending on the temperature coefficient of chain dimensions in the species.

Both mechanisms lead to thermorheological complexity for branched polymer liquids and are able to account for differences in such behavior among polymer species. Both operate in the same direction, and it is not clear how to distinguish them experimentally. We assume that each contributes to the observed behavior.

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Stereochemistry of Poly(1,3-cyclohexadienes). NMR Investigation of Effects due to the Solvent Medium and to the Mechanism of Polymerization

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ABSTRACT: The ^{13}C NMR and ^{1}H NMR spectra of poly(1,3-cyclohexadiene) (PCHD) were analyzed. Anionically polymerized samples, cationically polymerized samples, and samples polymerized with a Ziegler–Natta catalyst were investigated. The ^{1}H NMR and ^{13}C NMR spectra were taken at 270 and 67.88 MHz, respectively. The resolution of the former spectra was incomplete and they were deconvoluted by computer simulation. Relative intensities of the computer-resolved ^{1}H NMR peaks were used in the calculation of the isomeric composition of the investigated PCHD's. ^{1}H NMR results were confirmed qualitatively by ^{13}C NMR results. 3,3′-Bicyclohex-1-enyl (BCH) was used as a model compound for the verification of the proposed assignment of the experimentally observed chemical shifts. The effect of solvents on the microstructure of the anionically polymerized 1,3-cyclohexadiene has been found to be essentially analogous to that observed for the acyclic dienes. Significant differences were, however, detected. For example, even in polar solvents the fraction of 1,2 isomers did not exceed 50%. Apparently, steric hindrance precludes the formation of long sequences of 1,2 units. The formation of intermittent 1,2 and 1,4 sequences is feasible and their fraction increases with increasing temperature. The anionic polymerization of 1,3-cyclohexadiene in hexane and in bulk yields the 1,4 isomer in a predominantly cis-type planomeric conformation. The stereoselectivity of the cationic and the Ziegler–Natta systems is lower than that of the anionic ones.

Introduction

Polymers and copolymers of acyclic dienes have been thoroughly investigated, and the effect of the conditions of polymerization on their structural features has been elucidated.[1] Much less is known about polymers of their cyclic analogue 1,3-cyclohexadiene (CHD).

Several applications of poly(cyclohexadienes) (PCHD) were proposed, and knowledge of their microstructure is of considerable interest. It has been shown, for example, that the copolymer of CHD and pentadiene acts as an active ingredient of photomicrolithographic screens, and the optical resolution of such devices is greatly enhanced

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