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Dynamic Viscoelastic Characterization of a Polyurethane Network Formation

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ABSTRACT: The evolution of the frequency dependence of the viscoelastic properties during the gel formation of polyurethane has been monitored as a function of time. Over the frequency range investigated, the frequency dependence of the shear moduli G' and G'' are well described by the power laws $G' \sim \omega^{\Delta'}$ and $G'' \sim \omega^{\Delta''}$, for all the reaction times investigated. Gel times are taken as the critical times where a frequency independent loss tangent ($\tan(\delta) = G''/G'$) is observed. At these critical times, the frequency dependencies of G' and G'' follow the same power law with the same exponent $\Delta' = \Delta'' = 0.69 \pm 0.04$, which, within the experimental error, is independent of the initial stoichiometry r. Measurements of fully cured networks (far above the gel point) show that G'' follows a power law behavior with exponent $\Delta'' = 0.54$, while in the same frequency range, G' has already reached its plateau value. This low-frequency behavior of G'' appears to be independent of r (for $r > 0.6$) and is not as yet included in the theoretical models.

Introduction

Studies of dynamic properties of gelling systems using dynamic light scattering[1] and rheological measurements[2−16] have revealed that incipient or critical gels, i.e., systems at the gelation threshold, exhibit a continuous power law relaxation time spectrum. Measurements on critical gels of polyurethane,[2,3] polyester,[4] epoxy,[5−8] siloxane,[9,10] silica,[11,12] polycaprolactone,[13] poly(vinyl chloride),[14] pectin,[15] and gelatin[16] have clearly shown this power law behavior. However, only a few systems have been investigated during the whole process of the network formation, i.e., from the initial state of mixing the reactants until the fully cured network state. The characterization of the network buildup is very useful from both a theoretical and a practical point of view. The present experimental study concerns the characterization of dynamic viscoelastic properties as a function of reaction time during polyurethane gel formation and is mainly focused on three aspects: (i) determination of particular reaction times which can be viewed as gel points on the basis of the frequency dependence of the shear modulus, (ii) characterization of the frequency dependence of the shear modulus as a function of reaction time especially around the gel point and also for some fully cured samples, and (iii) study of the effect of the initial stoichiometric ratio on the frequency dependence of the shear modulus at both the gel time and the final state.

A theoretical model[17−19] of the evolution of the viscoelastic properties characterized by the complex shear modulus $G^* = G' + iG''$ is classically described by the following relation:

$$G^* = G_o\epsilon^t f(i\omega/\omega^*) \qquad (1)$$

Here $\epsilon = (p_c - p)/p_c$ is the relative distance to the gel point, p the reaction extent, and p_c the reaction extent at the gel point; $\omega^* = \omega_0\epsilon^{s+t}$ is the characteristic frequency associated with the slowest relaxation process; s and t are the exponents which govern the power law behaviors of the steady-state viscoelastic properties, i.e., the zero frequency viscosity, η_s, before the gel point and the zero frequency elasticity, G_s, above the gel point, respectively: $\eta_s = \eta_0\epsilon^{-s}$ and $G_s = G_0\epsilon^t\cdot\eta_0$, G_0 and ω_0 are related to local molecular properties (probed in the high-frequency domain) and are system dependent. Equation 1 allows one to model the frequency behavior of the material.

In this phenomenological framework, for $\omega < \omega^*$ and before the gel point ($p < p_c$), the material behaves as a viscous liquid and we have $f(i\omega/\omega^*) = (i\omega/\omega^*) + (\omega/\omega^*)^2 + ...$ which leads to:

$$G^* = (G_o/\omega_o^2)\epsilon^{-2s+t}\omega^2 + i(G_o/\omega_o)\epsilon^{-s}\omega \qquad (2)$$

We recover the two well-known power laws $G' \sim \omega^2$ and $G'' \sim \omega$.

After the gel point ($p > p_c$), we have $f(i\omega/\omega^*) = 1 + (i\omega/\omega^*) + ...$ which leads to:

$$G^* = G_o\epsilon^t + i(G_o/\omega_o)\epsilon^{-s}\omega \qquad (3)$$

The material behaves like an elastic medium with a storage modulus which is frequency independent while G'' keeps the same frequency dependence: $G'' \sim \omega$.

For $\omega_0 > \omega > \omega^*$, at any reaction extent, we have $f(i\omega/\omega^*) = (i\omega/\omega^*)^\Delta$, which leads to:

$$G^* \sim (i\omega/\omega_o)^\Delta \sim (\omega/\omega_o)^\Delta e^{i\Delta\pi/2} \sim (\omega/\omega_o)^\Delta e^{i\delta} \qquad (4)$$

where δ is the loss angle defined as

$$\delta = \arctan(G''/G') \qquad (5)$$

This frequency range corresponds to an excitation of the sample at a frequency higher than the characteristic frequency, ω^*, associated with the largest cluster. Therefore the modulus should be independent of this cluster size and thus of the relative distance to the gel point. At the gel point, ω^* tends to zero and the following power law is predicted in all the frequency ranges below ω_0:

$$G' \sim G'' \sim \omega^\Delta, \text{ with } \Delta = 2\delta/\pi \qquad (6)$$

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To summarize, in this so-called critical gelation domain, one expects according to the above model: (i) moduli independent of the reaction extent, (ii) a loss angle independent of frequency and reaction extent, and (iii) power law behavior for G' and G'' with the same exponent Δ.

Although the general mathematical framework is the same, the exponent Δ which governs the scaling expression in eq 4 will have different values according to different theoretical approaches to the dynamics of branched polymers near the gelation threshold. There are two main approaches: the electrical analogy and the Rouse model. In the electrical analogy first proposed by de Gennes,[20] numerical simulations in three dimensions predict $\Delta = 0.72 \pm 0.02$,[21–24] while for the Rouse model, which assumes no hydrodynamic interactions between clusters, $\Delta = 2/3$.[25,26] Experimental results for Δ reported in the literature on both chemical gels[2–13] and physical gels[14–16] vary between 0.50 and 0.73. In addition, for some particular systems,[9,27,28] the values of Δ are found to be strongly dependent on the initial stoichiometric ratio, as well as on the concentration and the molar mass of the starting material.

Experimental Section

Material and Sample Preparation. Polyurethanes (PU) were synthesized by condensation of poly(oxypropylene triol) with hexamethylene diisocyanate (HMDI). The polyols used in this study are propylene oxide adducts of trimethylolpropane. The number-average molar mass of the triol is 700 g/mol, and the hydroxyl content is found to be 4.16×10^{-3} mol/g, which leads to an effective functionality of the polyol close to 3. The stoichiometric ratio, r, is defined as the initial ratio of isocyanate groups, [NCO], to hydroxyl groups, [OH]. The stoichiometric ratios studied were the following: $r = 0.65$, 0.70, 0.80, 0.85, 0.90, and 0.99. After mixing the dried triol with HMDI in the appropriate stoichiometric ratio, 2×10^{-3} g of dibutyltin dilaurate catalyst was added for every 1 g of HMDI in the form of a 2% (w/w) solution in toluene. After mixing and complete homogenization of the reaction components, the sample was cured at 40 °C before being transferred to the rheometer which was thermostated at 22° ± 0.2C.

Rheological Experiments. Small strain oscillatory shear measurements were performed using a Rheometrics RDA II dynamic spectrometer with parallel-plate geometry. Strains between 0.02 and 0.5 s^{-1} were applied to provide an accurate torque response (at least 0.1% of maximum torque). The material was shown to behave linearly at these levels. A series of frequency sweeps during the cross-linking of the sample gave values for the shear modulus at various reaction extents in the vicinity of the gel point. The frequency sweeps were performed over 2 decades from 0.5 to 50 rad/s logarithmically spaced. Results obtained by the in situ technique compared favorably with results obtained on quenched samples, i.e., unbalanced stoichiometric polyurethanes (with $r < 1$) at complete consumption of NCO groups. For the fully cured samples, time–temperature superpositions were used to construct master curves with $T_{ref} = 303$ K.

Results and Discussion

Determination of the Gel Point. Figure 1 shows the dynamic storage modulus, G' (see Figure 1a), and the dynamic loss modulus, G'' (see Figure 1b), as a function of reaction time near the gel point for a PU sample with a stoichiometric ratio of $r = 0.85$ for several frequencies. As the measurements were performed at different frequencies, the data were not obtained at the same reaction time. A frequency scan starting at the lowest frequency took about 2 min. The experimental data, which are discrete and nonsimultaneous, have been fitted by a second-order polynomial function. The fitted curves are used to obtain $G'(\omega)$ and $G''(\omega)$ at equal reaction times.

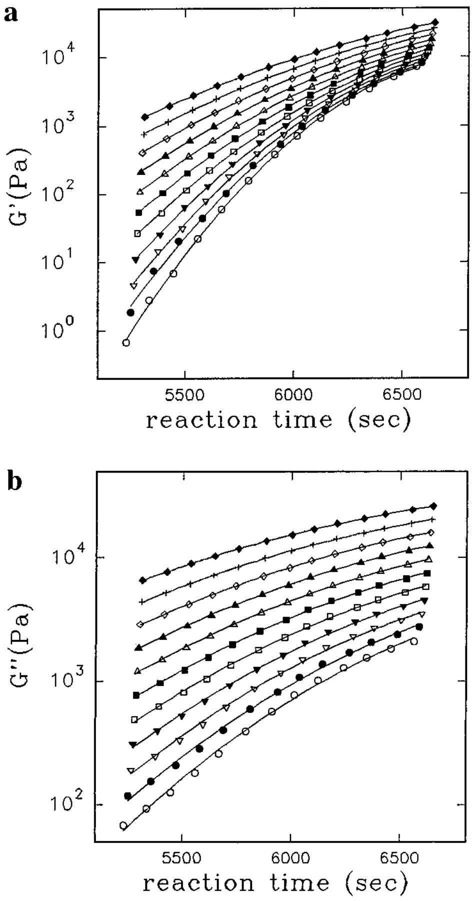

Figure 1. Evolution of the storage (a) and the loss (b) shear moduli as a function of the reaction time around the gel point for a PU with $r = 0.85$ obtained at different frequencies: $\omega =$ 0.5 (○), 0.792 (●), 1.26 (▽), 1.99 (▼), 3.15 (□), 5 (■), 7.92 (△), 12.6 (▲), 19.9 (◇), 31.5 (+), and 50.0 (◆) rad/s.

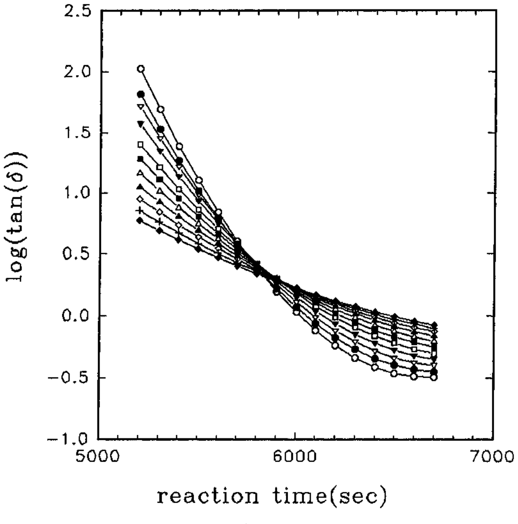

Figure 2. Evolution of tan(δ) as a function of reaction time around the gel point for a PU with $r = 0.85$ at different frequencies. The symbols are the same as in Figure 1.

Winter et al. have suggested that the gel point (or the gel time) corresponds to the extent (or the time) of reaction required to reach a frequency independent loss angle ($\tan(\delta) = G''/G'$).[29,30] Figure 2 clearly shows a coincidence domain of the time evolution of the tan δ curves obtained at different frequencies, localizing the gel point to the time range between 5700 and 6000 s.

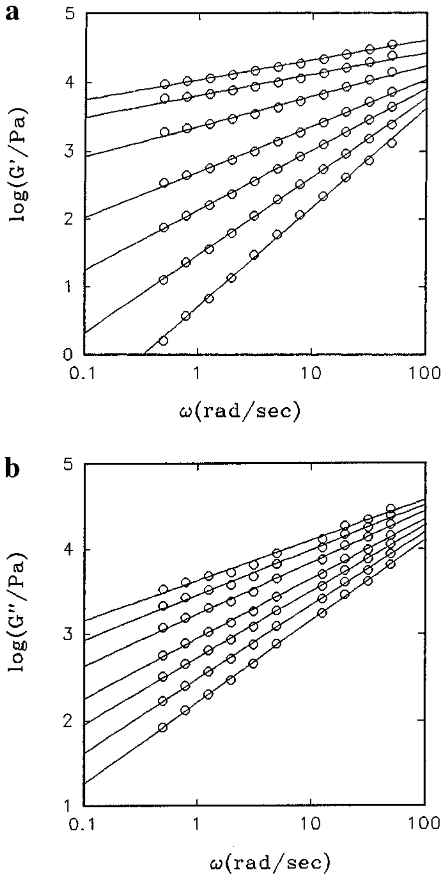

Figure 3. Frequency dependence of the storage (a) and the loss (b) shear moduli for a PU with $r = 0.85$ at different reaction times. From bottom to top, t = 5300, 5500, 5700, 5900, 6100, 6400, and 6700 s.

However, even for the highest frequency tested, we did not observe an independence of tan(δ) with reaction time as predicted by eq 6. The tan(δ) value corresponding to the critical reaction time t_{g1} = 5850 s is 2.1. Using this value of tan(δ) in eq 6 leads to the following value of the exponent Δ: $\Delta_1 = 0.71$. The absolute values of t_g do not have much significance because they depend strongly on the concentration of catalyst and the reaction temperature.

Frequency Dependence of the Shear Modulus as a Function of the Reaction Time. Figure 3 shows the frequency dependence of G' and G'' at different reaction times. Over the frequency range investigated (2 decades), the frequency dependence of the moduli are well described by power laws for all reaction times:

$$G' \sim \omega^{\Delta'} \qquad (7)$$

$$G'' \sim \omega^{\Delta''}$$

At the critical reaction time t_{g1} = 5850 s, G' and G'' follow nearly the same power laws: $\Delta'_2 = 0.73$ and $\Delta''_2 = 0.72$ (see Figure 4).

Figure 5 shows that the time evolutions of the exponents Δ' and Δ'' are continuous and smooth. The crossing point of these curves gives an alternative estimate for the critical reaction time t_{g3} = 5840 s and exponent $\Delta_3 = 0.73$. These different estimates of critical times and critical exponents indicate the relative precision with which these parameters may be determined (see Table 1).

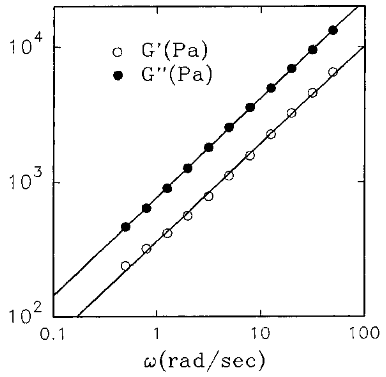

Figure 4. Frequency dependence of G' (○) and G'' (●) at the critical reaction time t_{g1} = 5850 s for a PU with $r = 0.85$.

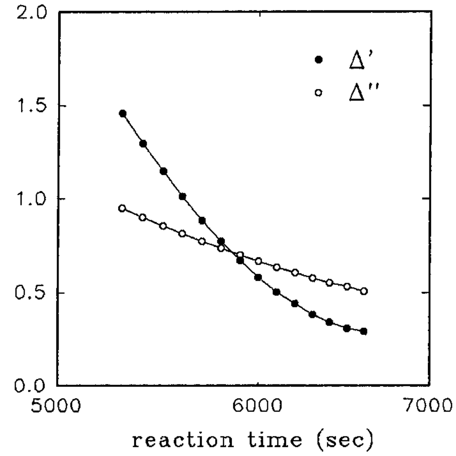

Figure 5. Evolution of the exponents Δ' (●) and Δ'' (○) obtained from the power law frequency dependence of G' and G'', respectively, as a function of the reaction time for a PU with $r = 0.85$.

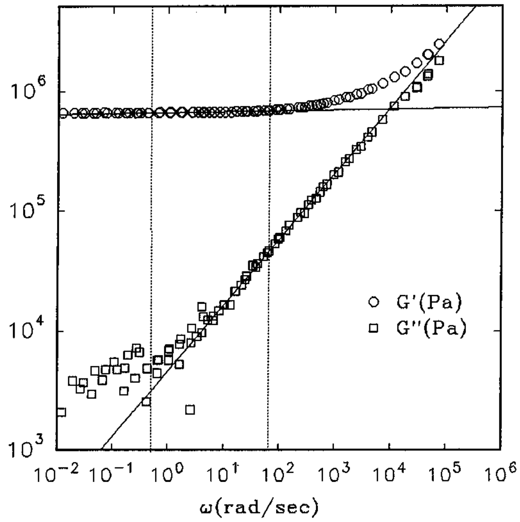

Figure 6. Frequency dependence of the storage and the loss shear moduli for a fully cured PU network with $r = 0.85$.

As already seen in Figure 3a, the limiting behavior of the dynamic storage modulus G' indicates that the system behaves like a Newtonian liquid before the gel point ($G' \sim \omega^2$) and tends to the behavior of a classical network ($G' \sim \omega^0$) after the gel point as predicted by the model above. If the dynamic storage modulus G' obeys the model predictions, it is not the same for the loss modulus G'' beyond the gel time. In fact, as shown in Figure 5, Δ'' continues to decrease gradually after the gel time instead of increasing again toward unity as predicted by the model. The fully cured network G'' follows a power law behavior with exponent Δ'' = 0.54,

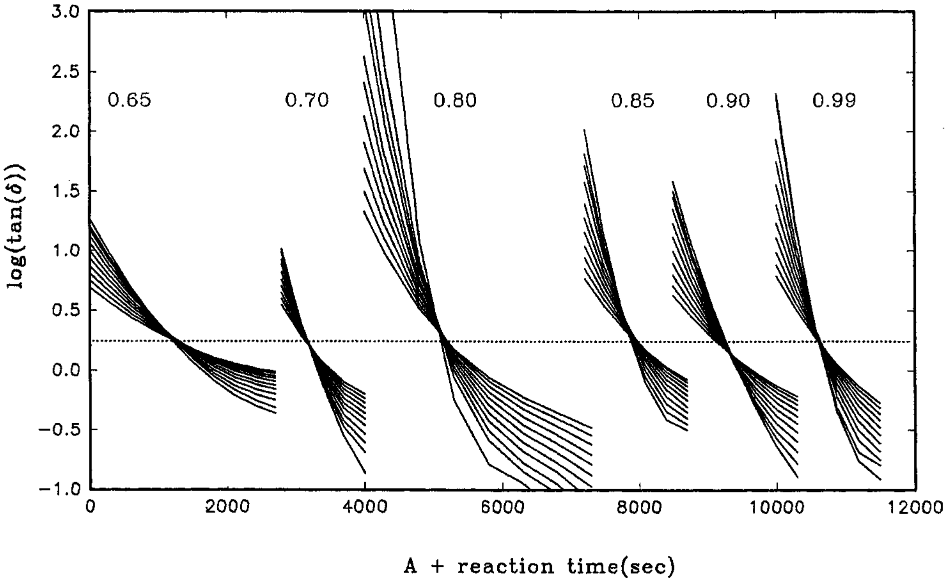

Figure 7. Evolution of tan(δ) as a function of the reaction time around the gel point at different frequencies for PU with the stoichiometric ratios indicated in the figure. *A* is an arbitrary time shift factor.

Table 1. Different Values of the Exponent Δ[a]

	$r = \frac{[\mathrm{NCO}]}{[\mathrm{OH}]}$					
	0.65	0.70	0.80	0.85	0.90	0.99
Δ_1	0.70	0.65	0.71	0.72	0.65	0.70
Δ'_2	0.70	0.65	0.72	0.73	0.65	0.70
Δ''_2	0.70	0.65	0.71	0.72	0.65	0.70
Δ_3	0.70	0.64	0.72	0.73	0.65	0.69

[a] Δ_1, from the crossing point of the time evolution of the tan δ curves which occurs at the critical reaction time t_{g1}; Δ'_2 and Δ''_2, from the frequency dependence of *G′* and *G″* at t_{g1}; Δ_3, from the crossing point of the time evolution of Δ′ and Δ″ which occurs at the critical reaction time t_{g3}.

while in the same frequency range *G′* has already reached its plateau value (see Figure 6). This intriguing aspect has earlier been observed by Adolf and Martin[31] for epoxy gels and is explained by these authors by the "persistence of remnant-collapsed or interpenetrating fractal domains formed at the gel point in the fully cured networks".

Influence of the Stoichiometric Ratio. To determine the influence of the stoichiometric ratio $r = [\mathrm{NCO}]/[\mathrm{OH}]$ on the gel point and on the frequency dependence of the complex zero frequency shear modulus as a function of the reaction time, we studied systems with $r = 0.65$, 0.70, 0.80, 0.85, 0.90, and 0.99. The behavior at different stoichiometries is very similar to that of $r = 0.85$. Figure 7 shows the evolution of the loss angle as a function of reaction time at different stoichiometries. It is clear that the value at the crossing point of the time evolution of the tan(δ) curves does not depend on the stoichiometric ratio in a systematic way. This observation is contrary to some experimental results reported in the literature[9,27,28] on other systems which show a dependence of the viscoelastic exponent at the gel point on the stoichiometry. The scatter of the values of Δ_1 (see Table 1) obtained for the different stoichiometric systems is more likely due to a lack of reproducibility of the experiments than to a systematic variation with stoichiometric ratio.

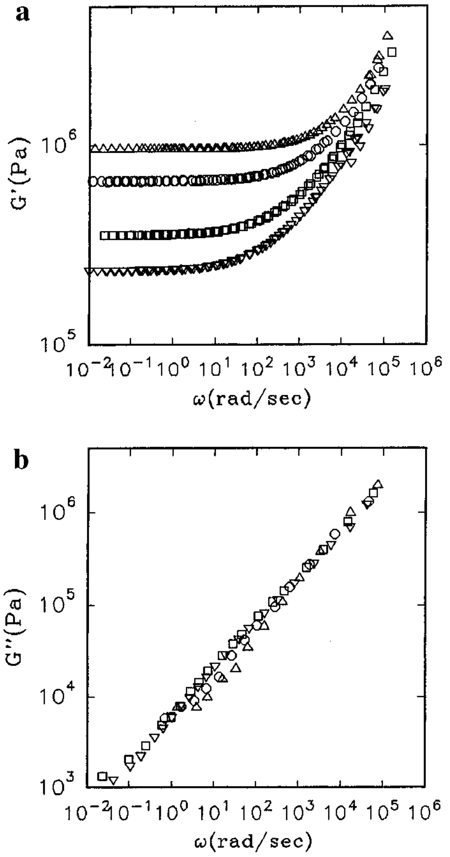

Figure 8. Frequency dependence of the storage (a) and the loss (b) shear moduli *G′* for fully cured PU networks with $r = 0.70$ (▽), 0.75 (□), 0.85 (○), and 0.90 (△).

In Table 1 the values of Δ are collected for different stoichiometric ratios determined using the three procedures described above: Δ_1 from the crossing point of the time evolution of the tan(δ) curves which occurs at the critical reaction time t_{g1}, Δ'_2 and Δ''_2 from the frequency dependence of *G′* and *G″* at the critical reaction time t_{g1}, and Δ_3 from the crossing point of the time dependence of the exponents Δ′ and Δ″ which occurs at the critical reaction time t_{g3}. The mean value of the exponent $\Delta_m = 0.69 \pm 0.04$ is consistent with the theoretical predictions of both the electrical model and the Rouse model. We note that the values obtained by varying the stoichiometric ratio of fully cured systems (see ref 2) are the same within the experimental error: $\Delta'_2 = \Delta''_2 = 0.69 \pm 0.02$. The values of t_{g1} and t_{g3} are very close for a given system, but the dependence on r is not significant as the catalyst concentration and curing history were not quite the same.

Finally, Figure 8 shows a preliminary study of the frequency dependence of the viscoelastic properties of fully cured networks for different stoichiometric ratios. As expected, the stoichiometry strongly affects the final storage modulus of the network which increases as the cross-linking density increases with increasing r (see Figure 8a). However, the low-frequency power law behavior of G'' appears independent of r for $r > 0.6$ (see Figure 8b). The slope is 0.54 ± 0.02 for $\omega < 10^3$ rad/s. There appears to be an additional frequency dependent component of the shear modulus in addition to the gel modulus. The low relative amplitude of this component at low frequencies makes it difficult to detect when measuring G', but it is clearly observed when measuring G''. This additional component is not discussed by the theoretical models summarized above and is as yet not properly understood.

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