40% conversion, k_t began to decrease rapidly toward 7.94 $\times 10^3$ dm³ mol⁻¹ s⁻¹ at 93.8% conversion, which is less than the k_t at 6.1% conversion by a factor of 2×10^3 . The steep decrease in kt corresponded to an increase in the viscosity of the polymerization mixture.

Thus, the present study revealed that the concentration of the poly(St) radical gradually increased to 30% conversion with small changes in the rate constants. The abrupt decrease in k_t arising from an enhanced viscosity of the polymerization system results in acceleration of the polymerization and an increase in \bar{M}_n of the polymer at high conversions. As a distinction from MMA polymerization, 6,7 the present polymerization yielded a poly(St) much shorter than poly(MMA). The chain length of the poly(St) radical was probably too short to suppress diffusion, forming an entanglement.¹³ Therefore, acceleration of polymerization caused by a considerable decrease in k_t is observed in the final stages of St polymerization and the conversion reaches almost 100%. While the change in k_p with conversion to MMA polymerization has been interpreted by the restricted diffusion of the polymer radical and monomer arising from lowering the $T_{\rm g}$, 7,8 $k_{\rm p}$ remained constant from the initial to final stages of St polymerization.

Buback and Schweer have concluded that k_p for ethylene is identical with the rate constant for addition of the C₁₀ radical or above to ethylene irrespective of chain length.¹⁴ However, if a slower diffusion of the poly(St) radical, which is less reactive than the poly(ethylene) radical, could differentiate from a low molecular weight homologue, the k_p and k_t values at the low-conversion range would exhibit dependencies on chain length.

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CORRECTIONS

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An error in computation was pointed out by Dr. Karen I. Winey, AT&T, Bell Laboratories, Murray Hill, NJ. The numerical values of Ψ_{PI} (SC) in Table II should read 0.1911 for B2 and 0.0806 for B2:H6 = 1:1, instead of 0.0678 and 0.0284, respectively, which suggests that the spheres are packed in a SC lattice rather than a BCC lattice for B2:H6 = 1:1. The packing symmetry of spheres in B2 cannot be uniquely determined by the volumetric consideration of this kind. This change does not alter the conclusions of the article.