heptenes in several of the oligomer samples. The C_{12} and C_{16} olefin oligomers gave gas chromatograms that appeared far too complex for specific oligomer identifications; thus only the C_8 distributions were investigated. As observed in the octenyllithium adducts,[1] hydrolysis yields primarily the 1,4 addition product irrespective of the incipient modes of butadiene addition as indicated by a comparison of the 1,4 percentages between α units for the C_8 and that of the C_{12}, C_{16}, and C_{20} oligomers. The C_8 1,4 content in Table II includes both *cis* and *trans* isomers as measured directly from the gas chromatograms of the various octenes. The most striking example of a change in the α configuration with hydrolysis was in sample 1-C. The 1,4 percentage among the octenes was 92 whereas the C_{12}, C_{16}, and C_{20} oligomers contained only 20–40% 1,4 configurations among the α units.

Conclusions

The observation that the oligomer distributions conformed to the Markov chain statistics proved very useful since glpc assignments could be made as a direct consequence[3] and each step of the oligomerization process subsequently characterized. The transition probabilities can be used to calculate "final polymer" compositions under carefully controlled reaction conditions, thus allowing the reaction conditions to be directly related to the incipient polymer microstructure. The sensitivity of the polymer microstructure to changes in reaction conditions precludes a similar but meaningful study of butadiene polymers. The second-order effects of the oligomerization processes were clearly indicated by a comparison of the compositions of the first monomer unit for the C_{12}, C_{16}, and C_{20} oligomers; however, the penultimate and ultimate effects upon the oligomer microstructure are small by comparison with experimental variables.

A polymerization mechanism involving butadiene addition to an alkenyllithium ion pair does not appear favorable in view of the nmr studies of the octenyllithium adducts and the product distributions *vs.* reaction conditions. There can be little doubt, however, that a two-step process is necessary before a reacting monomer unit assumes a particular configuration: (1) addition to form an alkenyllithium adduct which (2) assumes a configuration only after removal of the lithium atom through either a propagation or termination step.

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Computer Simulation of the Polymerization of Styrene. The Mechanism of Thermal Initiation and the Importance of Primary Radical Termination[1]

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ABSTRACT: We here report a computer simulation of the polymerization of styrene at 60°. Both the spontaneously initiated "thermal" polymerization and initiation by azobisisobutyronitrile and benzoyl peroxide have been studied by the use of the REMECH program of DeTar.[18] The primary aim of this study is to elucidate the mechanism of the thermal polymerization of styrene and to test the mechanism proposed by Mayo.[8] The Mayo mechanism postulates the reversible formation of a Diels–Alder dimer, AH, between two styrene molecules and the reaction of AH with a third sytrene molecule to form radicals. Values of k_{ith}, k_{p}, and k_{t} are known from the literature as are R_{ith}, R_{Pth}, and $\bar{P}_{\mathrm{n}}$. (Rate constants are defined in Schemes I–III.) We have assigned values to K_{DA}, k_{fDA}, k_{rDA}, k_{MIH}, and k_{trAH}; the concentration of AH as a function of conversion was calculated by the program. We have reassigned a more reasonable value to k_{trM} and our treatment explains why the experimentally measured value for the apparent transfer constant of monomer is unreasonable. Our study also makes some predictions about the thermal mechanism. The program also allows the measurement of the importance of primary radical termination (PRT) in initiated polymerization. Primary radical termination is the reaction in which initiator radicals terminate growing chains rather than adding to monomer to initiate chain growth. We have evaluated k_{PRT} and the fraction of the chain ends formed by PRT for styrene.

A number of systems are known in which free radicals are produced at greatly enhanced rates from the interaction of normal organic molecules. This fascinating phenomenon, called molecule-induced homolysis, has been reviewed[3] and, at least in some cases, is well understood. The self-initiated "thermal" polymerization of styrene is perhaps the earliest known example of this phenomenon, and its mechanism still is not known with certainty.

Carefully and exhaustively purified styrene undergoes

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(1) (a) Reactions of Radicals. XXXIII. (b) We wish to acknowledge partial support of this work by the U. S. Army Research Office (Durham).

(2) Predoctoral NASA Trainee, 1966–1969, LSU.

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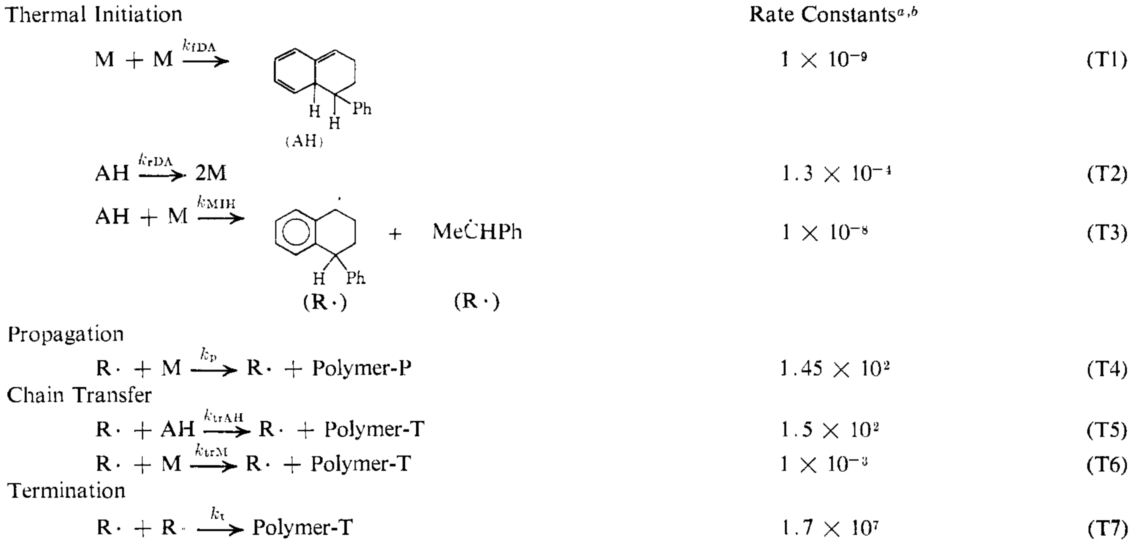
SCHEME I

MECHANISM AND RATE CONSTANTS FOR THERMAL POLYMERIZATION OF STYRENE AT 60°



Thermal Initiation	Rate Constants[a,b]	
$M + M \xrightarrow{k_{fDA}}$ (AH)	1×10^{-9}	(T1)
$AH \xrightarrow{k_{rDA}} 2M$	1.3×10^{-4}	(T2)
$AH + M \xrightarrow{k_{MIH}}$ (R·) + $Me\dot{C}HPh$ (R·)	1×10^{-8}	(T3)
Propagation		
$R\cdot + M \xrightarrow{k_p} R\cdot + \text{Polymer-P}$	1.45×10^{2}	(T4)
Chain Transfer		
$R\cdot + AH \xrightarrow{k_{trAH}} R\cdot + \text{Polymer-T}$	1.5×10^{2}	(T5)
$R\cdot + M \xrightarrow{k_{trM}} R\cdot + \text{Polymer-T}$	1×10^{-3}	(T6)
Termination		
$R\cdot + R\cdot \xrightarrow{k_t} \text{Polymer-T}$	1.7×10^{7}	(T7)

[a] Units are M^{-1} sec^{-1} except for step T2 which is in sec^{-1}. [b] Values of k_p (T4) and k_t (T7) are literature values.

polymerization at a reproducible rate of about 0.1%/hr at 60° and 16%/hr at 130°.[4] It is known that radicals are involved in this process since inhibitors prevent the reaction and free-radical polymerization kinetics correctly explain the results.[5] In 1937, Flory[5a] suggested that this polymerization is initiated by combination of two styrene molecules to produce a diradical. However, statistical calculations by Haward[6a] and Zimm[6b] and studies conducted on diradical initiators by Tobolsky[7a] and Overberger[7b] some time ago, and more recently by Kopecky,[7c] indicate that diradicals cyclize too rapidly to initiate the polymerization of styrene.[7d]

The mechanism for this reaction which has received the most support was proposed by Frank Mayo[8] in 1961 (Scheme I). The first step in the mechanism is the Diels–Alder dimerization (eq T1) to form 1-phenyl-1,2,3,9-tetrahydronaphthalene (AH). In a subsequent step, AH reacts with a third styrene molecule in a molecule-induced homolysis (eq T3) to produce a styryl and a 1-phenyltetralyl radical. These two radicals then initiate polymerization, and propagation and termination occur as usual.[9–13] The driving force for the molecule-induced homolysis step is the aromatization of AH to form the 1-phenyltetralyl radical. Mayo[8] suggested this mechanism to rationalize the observation that the rate of thermal polymerization (R_{Pth}) is $^5/_2$-order in monomer, which implies that the initiation is third order, and the isolation of substantial amounts of 1-phenyltetralin from solutions of styrene which were heated for long periods in the presence of various inhibitors.[14a]

Hiatt and Bartlett[15] have confirmed the third-order nature of the initiation step, and 1-phenyltetralin has been isolated from uninhibited thermal polymerizations.[14] The kinetic isotope effects observed using deuterium-substituted styrenes are consistent with the Mayo mechanism.[16]

Recently, indirect support of this mechanism has been published by a group of Japanese workers.[17] They allowed 2-vinylfuran and 2-vinylthiophene to polymerize in the absence of initiators and isolated the rearranged, aromatized products[14a] from the Diels–Alder dimerization of these monomers. They suggest

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that all vinyl aromatics undergo self-initiated polymerization by a mechanism similar to that proposed for styrene.

We here report a simulation of the polymerization of styrene by computer using the REMECH program of DeTar.[18] The primary aim of this study is to elucidate the mechanism of the thermal polymerization of styrene and, in particular, to test the mechanism originally proposed by Mayo.[8] Values of k_{ith}, k_p, and k_t are known from the literature as are R_{ith}, R_{Pth}, and $\bar{P}_n$. We have assigned plausible values to K_{DA}, k_{fDA}, k_{rDA}, k_{trAH}, and k_{MIH}, and the concentration of AH as a function of conversion was calculated by the program. We have reassigned a more reasonable value to k_{trM} and our treatment explains why the experimentally measured value for the apparent transfer constant of monomer is unreasonable. Our study also makes some predictions about the thermal mechanism. It is possible that a slightly different set of rate constants for the thermal polymerization could also simulate the observed results; however, our present set provides an interesting confirmation of the Mayo mechanism.

The program also allows the measurement of the importance of primary radical termination (PRT) in initiated polymerizations. In PRT, primary radicals from the initiator terminate growing chains rather than adding to monomer to initiate growth. It is generally accepted that PRT is one of the most important causes of the deviations of the kinetics of vinyl polymerization from the kinetic laws predicted from the simple system of equations.[12,13] Numerous authors[19] have studied PRT using various kinetic and algebraic equations but always under static and restrictive conditions. Use of computer simulation allows the study of PRT under more realistic conditions. We have evaluated k_{PRT} for two initiators and have measured the fraction of chain ends formed by PRT for styrene over a wide initiator concentration range.

We have tested the computer predictions using data for the thermal polymerization and also for polymerizations initiated by benzoyl peroxide and by azobisisobutyronitrile (AIBN).[19a,19b,20-34] Both these initiators have been extensively studied over wide concentration ranges, and they differ in their decomposition rates and chain transfer constants.[19a,19b,20,31-34] We have used a single rate constant for any given reaction in both the thermal and the initiated polymerizations.

Scheme I lists the reaction steps and rate constants which we have assigned to the steps of the Mayo mechanism, and Schemes II and III give the steps and rate constants for the polymerization initiated by benzoyl peroxide and AIBN. The computer utilizes products called Polymer-T and Polymer-P to allow the calculation of both the rates of polymerization and degree of polymerization. Polymer-P counts the number of styrene units that add to the growing polystyryl radical and Polymer-T counts the number of terminated polymer chains. The print-out tabulates the molarities of Polymer-P and Polymer-T at designated reaction times. The number average degree of polymerization $\bar{P}_n$ is calculated from the molarities of Polymer-P and Polymer-T by eq 1

$$\bar{P}_n = \frac{[\text{Polymer-P}]}{[\text{Polymer-T}]} = \frac{\text{no. of styrene units}}{\text{no. of polymer molecules}} \qquad (1)$$

and the rate of polymerization is calculated by eq 2.

$$R_P = \frac{-\mathrm{d}(M)}{\mathrm{d}t} = \frac{[\text{Polymer-P}]}{\text{reaction time}} \qquad (2)$$

Discussion and Results

Assignment of Rate Constants to the Steps in the Mayo Mechanism. Standard free-radical polymerization kinetics[9-13] give the following expressions for the rate of thermal polymerization

$$R_{\text{Pth}} = \frac{k_p(R_{\text{ith}})^{0.5}[M]}{(2k_t)^{0.5}} \qquad (3)$$

and the rate of thermal initiation

$$R_{\text{ith}} = 2k_{\text{MIH}}[\text{AH}][M] = 2k_{\text{ith}}[M]^3 \qquad (4)$$

The AH molarity is defined by steady-state approximation as

$$[\text{AH}] = \frac{k_{\text{fDA}}[M]^2}{k_{\text{rDA}} + k_{\text{MIH}}[M] + k_{\text{trAH}}(R_{\text{ith}}/2k_t)^{0.5}} \qquad (5)$$

The rate constants are defined in Scheme I. Values are known for the rates of thermal polymerization[20] and thermal initiation, and the equilibrium constant

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SCHEME II
BENZOYL PEROXIDE-INITIATED POLYMERIZATION OF STYRENE AT 60°

Initiation	Rate Constants[a,b]	
$2\mathrm{M} \xrightarrow{k_{\mathrm{fDA}}} \mathrm{AH}$	1×10^{-9}	(B1)
$\mathrm{AH} \xrightarrow{k_{\mathrm{rDA}}} 2\mathrm{M}$	1.3×10^{-4}	(B2)
$\mathrm{AH} + \mathrm{M} \xrightarrow{k_{\mathrm{MIH}}} 2\mathrm{R}\cdot$	1×10^{-8}	(B3)
$\mathrm{Bz_2O_2} \xrightarrow{k_{\mathrm{d}}f} 2\mathrm{BzO}\cdot$	2×10^{-6}	(B4)
$\mathrm{BzO}\cdot \xrightarrow{k_{\mathrm{dCO_2}}} \mathrm{Ph}\cdot + \mathrm{CO_2}$	4.8×10^{3}	(B5)
$\mathrm{BzO}\cdot + \mathrm{M} \xrightarrow{k_{\mathrm{i}}} \mathrm{R}\cdot$	1.2×10^{4}	(B6)
$\mathrm{Ph}\cdot + \mathrm{M} \xrightarrow{k_{\mathrm{i}}'} \mathrm{R}\cdot$	1×10^{5}	(B7)
Propagation		
$\mathrm{R}\cdot + \mathrm{M} \xrightarrow{k_{\mathrm{p}}} \mathrm{R}\cdot + \text{Polymer-P}$	1.45×10^{2}	(B8)
Chain Transfer		
$\mathrm{R}\cdot + \mathrm{AH} \xrightarrow{k_{\mathrm{trAH}}} \mathrm{R}\cdot + \text{Polymer-T}$	1.5×10^{2}	(B9)
$\mathrm{R}\cdot + \mathrm{M} \xrightarrow{k_{\mathrm{trM}}} \mathrm{R}\cdot + \text{Polymer-T}$	1×10^{-3}	(B10)
$\mathrm{R}\cdot + \mathrm{Bz_2O_2} \xrightarrow{k_{\mathrm{trI}}} \mathrm{BzO}\cdot + \text{Polymer-T}$	0.8×10^{1}	(B11)
Termination		
$\mathrm{R}\cdot + \mathrm{R}\cdot \xrightarrow{k_{\mathrm{t}}} \text{Polymer-T}$	1.7×10^{7}	(B12)
Primary Radical Termination		
$\mathrm{R}\cdot + \mathrm{BzO}\cdot \xrightarrow{k_{\mathrm{PRT}}} \text{Polymer-T}$	6×10^{9}	(B13)

[a] Units are M^{-1} sec^{-1} except for B2, B4, and B5 which are in sec^{-1}. [b] Literature values of rate constants for steps B4, B8, B11, and B12 were used.

SCHEME III
AIBN-INITIATED POLYMERIZATION OF STYRENE AT 60°

Initiation	Rate Constants[a,b]	
$2\mathrm{M} \xrightarrow{k_{\mathrm{fDA}}} \mathrm{AH}$	1×10^{-9}	(A1)
$\mathrm{AH} \xrightarrow{k_{\mathrm{rDA}}} 2\mathrm{M}$	1.3×10^{-4}	(A2)
$\mathrm{AH} + \mathrm{M} \xrightarrow{k_{\mathrm{MIH}}} 2\mathrm{R}\cdot$	1×10^{-8}	(A3)
$\mathrm{AIBN} \xrightarrow{k_{\mathrm{d}}f} 2\mathrm{IBN}\cdot$	6×10^{-6}	(A4)
$\mathrm{IBN}\cdot + \mathrm{M} \xrightarrow{k_{\mathrm{i}}} \mathrm{R}\cdot$	3×10^{3}	(A5)
Propagation		
$\mathrm{R}\cdot + \mathrm{M} \xrightarrow{k_{\mathrm{p}}} \mathrm{R}\cdot + \text{Polymer-P}$	1.45×10^{2}	(A6)
Chain Transfer		
$\mathrm{R}\cdot + \mathrm{AH} \xrightarrow{k_{\mathrm{trAH}}} \mathrm{R}\cdot + \text{Polymer-T}$	1.5×10^{2}	(A7)
$\mathrm{R}\cdot + \mathrm{M} \xrightarrow{k_{\mathrm{trM}}} \mathrm{R}\cdot + \text{Polymer-T}$	1×10^{-3}	(A8)
$\mathrm{R}\cdot + \mathrm{AIBN} \xrightarrow{k_{\mathrm{trI}}} \mathrm{R}\cdot + \text{Polymer-T}$	0.5×10^{1}	(A9)
Termination		
$\mathrm{R}\cdot + \mathrm{R}. \xrightarrow{k_{\mathrm{t}}} \text{Polymer-T}$	1.7×10^{7}	(A10)
Primary Radical Termination		
$\mathrm{R}\cdot + \mathrm{IBN}\cdot \xrightarrow{k_{\mathrm{PRT}}} \text{Polymer-T}$	8×10^{9}	(A11)

[a] Units are in M^{-1} sec^{-1} except for A2 and A4 which are in sec^{-1}. [b] Literature values of rate constants for steps A4, A6, A9, and A10 were used.

for the Diels–Alder dimerization, $K_{\mathrm{DA}} = k_{\mathrm{fDA}}/k_{\mathrm{rDA}} = 10^{-5.5}$, can be calculated by use of Benson's[22] method of additivity of group properties. The value of K_{DA} calculated in this manner is accurate to an order of magnitude, and was used only as a guide in assigning values to k_{fDA} and k_{rDA}.

In a free-radical polymerization there are several chain-ending processes which control the degree of polymerization ($\bar{P}_{\mathrm{n}}$). These include termination, transfer to monomer, transfer to initiator, transfer to any solvent which may be present, and primary radical termination (termination by combination of a growing chain and an initiator radical). The relation between the degree of polymerization and the chain-end forming processes is expressed by[19a]

$$1/\bar{P}_{\mathrm{n}} = \frac{k_{\mathrm{t}}R_{\mathrm{P}}}{k_{\mathrm{p}}^2[\mathrm{M}]^2} + C_{\mathrm{M}} + C_{\mathrm{S}}\frac{[\mathrm{S}]}{[\mathrm{M}]} + C_{\mathrm{I}}\frac{[\mathrm{I}]}{[\mathrm{M}]} + PRT \qquad (6)$$

where R_{P} is the rate of polymerization, C_{M} is the monomer transfer constant, C_{S} is the transfer constant

TABLE I
THERMAL POLYMERIZATION OF STYRENE AT 60°

						—% contribution to chain ends—			
Time, hr	Convn, %	$R_P \times 10^6$	[AH] × 10^4	$\bar{P}_n \times 10^{-3}$	$10^5/\bar{P}_n$	C_{AH}[AH]/[M]	C_M	Termination	$\bar{P}_w/\bar{P}_n$
1	0.038	0.903	2.129	29.3	3.42	47.5	20.2	32.5	1.87
2	0.100	1.20	3.454	20.4	4.90	56.5	14.1	29.6	1.90
3	0.173	1.38	4.279	16.9	5.94	60.5	11.6	27.8	1.91
4	0.252	1.51	4.792	14.9	6.68	62.7	10.3	26.7	1.92
5	0.335	1.60	5.109	13.9	7.19	64.3	9.6	26.1	1.91
6	0.420	1.67	5.304	13.2	7.59	65.3	9.1	25.6	1.91
7	0.506	1.73	5.423	12.6	7.91	66.0	8.7	25.2	1.93
8	0.592	1.77	5.493	12.3	8.13	66.7	8.5	25.1	1.91
9	0.678	1.80	5.533	12.0	8.34	66.9	8.3	24.9	1.92
10	0.765	1.82	5.555	11.8	8.50	67.3	8.1	24.7	1.91
11	0.851	1.85	5.565	11.6	8.62	67.5	8.0	24.6	1.92
12	0.938	1.87	5.567	11.5	8.72	67.6	7.9	24.4	1.92
13	1.03	1.88	5.565	11.4	8.81	67.8	7.8	24.4	1.92
14	1.11	1.90	5.560	11.2	8.89	67.9	7.8	24.4	1.92
16	1.28	1.91	5.545	11.1	9.03	68.1	7.7	24.2	1.92
18	1.45	1.93	5.528	11.0	9.12	68.2	7.6	24.1	1.92
20	1.63	1.94	5.509	10.9	9.14	68.4	7.5	24.1	1.93
30	2.47	1.96	5.415	10.7	9.34	68.7	7.4	24.0	1.93
40	3.29	1.97	5.324	10.6	9.43	68.5	7.3	23.9	1.93
50	4.10	1.96	5.235	10.6	9.43	68.7	7.3	23.9	1.93
75	6.04	1.93	5.024	10.6	9.44	69.0	7.3	23.9	1.93
100	7.89	1.89	4.826	10.6	9.41	68.7	7.3	23.9	1.93

of solvent S, C_I is the initiator transfer constant, and *PRT* is the ratio of the rate of primary radical termination to the rate of polymerization. For thermally initiated polymerization with no solvent, eq 6 becomes

$$1/\bar{P}_n = \frac{k_t R_{Pth}}{k_p^2(M)^2} + C_M + C_{AH}\frac{[AH]}{[M]} \qquad (7)$$

where C_{AH} is the transfer constant for AH and *PRT* is assumed to be negligible.[35] Müller[14b] and others[24] have observed that the degree of polymerization at low conversions of self-initiated runs is much higher than the plateau value obtained at higher conversions. To explain this anomalous behavior, Müller suggested that transfer to monomer controls the chain-end forming process at low conversions; however, as the AH concentration increases to a steady-state value, transfer to AH becomes the most important chain-end forming process, and at the steady state in AH a plateau value for the degree of polymerization is observed.

The transfer rate constant for AH is expected to be unusually large for a hydrocarbon since transfer allows aromatization. In this connection, Olaj[25] has pointed out that the chain transfer constant of styrene (6×10^{-5}) should be lower than the transfer constant of ethylbenzene[26] (8.3×10^{-5}) and closer to that observed for benzene[26] (6×10^{-6}). A lower value of the monomer chain transfer constant and a high value of C_{AH} suggests that the apparent transfer constant for styrene should be written as a sum

$$C_M(\text{apparent}) = C_M(\text{actual}) + C_{AH}\frac{[AH]}{[M]} \qquad (8)$$

where C_M(apparent) is the observed monomer chain transfer constant equal to 6×10^{-5}, and C_M(actual) is the true monomer chain transfer constant.[36]

Knowledge of the value of the degree of polymerization at different conversions and of the values R_{ith}, R_{Pth}, k_p, k_t, and K_{DA} enables us to assign reasonable values to k_{fDA}, k_{rDA}, k_{MIH}, k_{trAH} and k_{trM} steps in the Mayo mechanism shown in Scheme I. We used the value for the propagation rate constant k_p recommended by Walling.[27] The termination rate constant was calculated from the value of $k_t/k_p^2 = 800$.[10,28]

Agreement of Our Results with Reported Data. These rate constants lead to a rate of thermal initiation of 0.9×10^{-10} M^{-1} sec^{-1} at 60°, in excellent agreement with the observed value of 1.3×10^{-10} M^{-1} sec^{-1} reported by Russell and Tobolsky.[21] Our rate of thermal polymerization of 1.9×10^{-6} M sec^{-1} (Table I) compares with the average value of 2.04×10^{-6} M sec^{-1} obtained by Mayo, Gregg, and Matheson.[20]

The program gives a degree of polymerization which decreases from a high value of 2.93×10^4 at low conversions to a plateau value of 1.06×10^4 at high conversions in accordance with the observation of Müller[14b] and others[24] (Table I and Figure 1). Our plateau value of $\bar{P}_n$ lies between the average value of 0.9×10^4 observed by Mayo and the plateau value of 1.12×10^4 published by Loucheux.[24b]

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[35] In our studies *PRT* always is negligible at the low rates achieved by thermal initiation.

[36] It might appear that eq 3, 4, 5, and 7 and the known values of $1/P_n$, R_{Pth}, R_{ith}, k_{ith}, k_p, and k_t could be used in a simple calculation to give values for k_{fDA}, k_{rDA}, k_{MIH}, k_{trAH}, and k_{trM} or the AH concentration as function of conversion. However, use of the literature value of k_i or R_{ith} in eq 4 gives only the product k_{MIH}[AH]. If the calculated value of K_{DA} and the literature values of R_{ith} and k_t are used in eq 5 one still cannot separate or calculate any usable values of k_{MIH}, k_{trAH}, k_{fDA}, or [AH]. And use of the literature values of R_{Pth}, k_p, k_t, and C_M in eq 7 does not duplicate the characteristic behavior of $1/P_n$ for thermal polymerization. A computer program is necessary to duplicate the conditions of thermal polymerizations and satisfy eq 3–8.

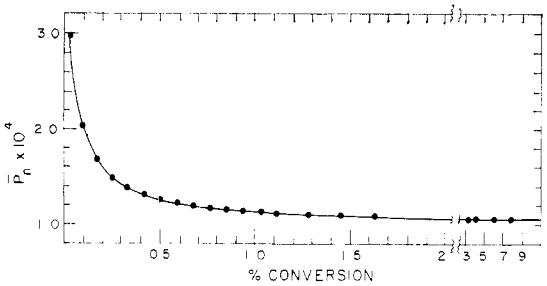

Figure 1. Graph of $\bar{P}_n$ *vs.* per cent conversion for the thermal polymerization of styrene at 60°. Data taken from Table I.

The computer print-out and the relations for converting number average to weight average degree of polymerization developed by Olivé and Olivé[26] enabled us to calculate[26b] the dispersion ($\bar{P}_w/\bar{P}_n$). The value of 1.93 at the plateau is in accord with the value of 1.879 found by Macosko and Weale.[29] The weight average molecular weight of 2.11 × 10^6, which is calculated from the dispersion and $\bar{P}_n$ values, duplicates the value of 2.25 × 10^6 reported by Boyer and Rubens.[30] The values assigned to the transfer rate constants of monomer and AH give a total value for C_M(apparent) in eq 8 of 7.5 × 10^{-5}, which is in excellent agreement with the observed value of 6 × 10^{-5}. The monomer chain transfer constant of 7 × 10^{-6} corresponds closely to the value for benzene of 6 × 10^{-6} and the value found for the AH chain transfer constant is 1.0.

Compatibility of the Thermal and Initiated Mechanisms of Polymerization. The expression for the rate of polymerization including both thermal initiation and the initiated rate is

$$R_p = \frac{k_p(R_i + R_{ith})^{0.5}[M]}{(2k_t)^{0.5}} \qquad (9)$$

where R_i equals $2k_d f[I]$ and R_{ith} equals $2k_{MIH}[AH][M]$. Substitution of eq 9 and the expressions for R_i and R_{ith} in eq 6 gives

$$1/\bar{P}_n = \frac{k_t(k_d f[I] + k_{MIH}[AH][M])^{0.5}}{k_p[M]} + C_M + C_{AH}\frac{[AH]}{[M]} + C_I\frac{[I]}{[M]} + PRT \qquad (10)$$

The value assigned to the rate constants for the thermal mechanism is quite critical at low initiator concentrations; at higher initiator concentrations the thermal polymerization is negligible and the value for k_{PRT} becomes important.

Assignment of the Rate Constants for the Benzoyl Peroxide-Initiated Polymerizations. The rate constants which duplicated the rate and degree of polymerization data and sources of chain ends (eq 10) for each benzoyl peroxide concentration are listed in Table II. We used the $k_d f$ value (6 × 10^{-6} sec^{-1}) reported by Mayo[21] and Tobolsky.[31] The values for the rate constants for the decarboxylation of the benzoyloxy radical (eq B5) and for addition of the benzoyloxy radical to styrene (eq B6) were assigned to agree with the reported[32] ratio k_{dCO_2}/k_i = 0.4. The value for the benzoyl peroxide transfer rate constant (eq B11) was calculated from the reported[20] chain transfer constant for benzoyl peroxide of 0.055 and the assigned value of k_p.

TABLE II

RATE CONSTANTS FOR THE REACTION STEPS IN THE INITIATED POLYMERIZATION

Benzoyl peroxide		AIBN	
Eq	Rate constant[a]	Eq	Rate constant[a]
Initiation			
B1	$k_{fDA} = 1 \times 10^{-9}$	A1	$k_{fDA} = 1 \times 10^{-9}$
B2	$k_{rDA} = 1.3 \times 10^{-4}$	A2	$k_{rDA} = 1.3 \times 10^{-4}$
B3	$k_{MIH} = 1 \times 10^{-8}$	A3	$k_{MIH} = 1 \times 10^{-8}$
B4	$k_d f = 2 \times 10^{-6}$	A4	$k_d f = 6 \times 10^{-6}$
B5	$k_{dCO_2} = 4.8 \times 10^{3}$	A5	$k_i = 3 \times 10^{3}$
B6	$k_i = 1.2 \times 10^{4}$		
B7	$k_i' = 1 \times 10^{5}$		
Propagation			
B8	$k_p = 1.45 \times 10^{2}$	A6	$k_p = 1.45 \times 10^{2}$
Chain transfer			
B9	$k_{trAH} = 1.5 \times 10^{2}$	A7	$k_{trAH} = 1.5 \times 10^{2}$
B10	$k_{trM} = 1 \times 10^{-3}$	A8	$k_{trM} = 1 \times 10^{-3}$
B11	$k_{trI} = 8$	A9	$k_{trI} = 5$
Termination			
B12	$k_t = 1.7 \times 10^{7}$	A10	$k_t = 1.7 \times 10^{7}$
Primary radical termination			
B13	$k_{PRT} = 6 \times 10^{9}$	A11	$k_{PRT} = 8 \times 10^{9}$

[a] Units are M^{-1} sec^{-1} except for B2, B4, B5, A2, and A4 which are sec^{-1}.

Assignment of Rate Constants to the Steps in AIBN-Initiated Polymerization. Table II contains a list of the assigned rate constants which duplicated reported data. For the AIBN decomposition step, we used the reported $k_d f$.[33]

Recently Pryor and Fiske[19a] and May and Smith[34] published values for the AIBN chain transfer constant that indicate, in contrast to earlier studies,[33] that AIBN chain transfers at approximately the same rate as benzoyl peroxide. We, therefore, assigned a value for the AIBN transfer rate constant (eq A9) which gives a $C_{AIBN} \cong$ 0.03, in agreement with the new value of C_{AIBN}.[19a, 34]

Because AIBN has a $k_d f$ value which is three times greater than that for benzoyl peroxide, it produces higher rates of polymerization at similar initiator concentrations.[19a, 19b, 20] Several authors[19a, 19b] have shown that because of this, primary radical termination occurs to a greater extent in AIBN than benzoyl peroxide. We assigned a value for the primary radical termination rate constants which agrees with these results.[19a, 19b]

Agreement of Our Results with Reported Data. For benzoyl peroxide-initiated polymerizations we have attempted to duplicate the experimental data of Mayo, Gregg, and Matheson[20] (Table III). Our values of the degree of polymerization and rate of polymerization agree with theirs to within 5% for most initiator concentrations.

We attempted to duplicate the results of Pryor and Fiske[19a] and Manabe, Utsumi, and Okamura[19b] for the AIBN-initiated polymerization. The agreement of our values with their rates and molecular weights at similar concentrations is within 10% (Table IV). We ascribe the poorer agreement of the AIBN data in comparison to benzoyl peroxide to the uncertainty in the AIBN transfer rate constant and in the primary radical termination rate constant.[19a]

TABLE III

BENZOYL PEROXIDE-INITIATED POLYMERIZATION OF STYRENE AT 60°

Time, sec	$[Bz_2O_2]$, M	$R_p \times 10^5$		$10^5/\bar{P}_n$		$\bar{P}_n \times 10^{-3}$	$\bar{P}_w/\bar{P}_n$
		This work[a]	Ref 20[b]	This work	Ref 20[b]		
1.65×10^5	1×10^{-4}	0.41		11.9		8.38	1.83
1.5×10^5	1.25×10^{-4}	0.46	0.5	12.4	12.1	8.05	1.81
1.09×10^5	2.5×10^{-4}	0.63	0.69	14.4	14.7	6.95	1.76
7.80×10^4	5×10^{-4}	0.88	0.93	17.3	16.6	5.77	1.71
5.52×10^4	1×10^{-3}	1.24	1.3	21.8	21.5	4.58	1.67
3.49×10^4	2.5×10^{-3}	1.97	2.05	30.8	30.5	3.24	1.58
2.46×10^4	5×10^{-3}	2.79	2.74	41.8	42.4	2.39	1.60
1.74×10^4	1×10^{-2}	3.95	3.99	58.4	61.7	1.71	1.60
1.23×10^4	2×10^{-2}	5.59	5.6	84.1	85.8	1.19	1.61
8.68×10^3	4×10^{-2}	7.93	8.1	124.6	128.0	0.802	1.63
6.14×10^3	8×10^{-2}	11.2	11.2	190.4	197.0	0.525	1.65
5.50×10^3	1×10^{-1}	12.5		219.5		0.456	1.67
4.35×10^3	1.6×10^{-1}	15.8	16.4	299.4	297.0	0.334	1.70

[a] All runs made to 8% conversion. [b] Data were averaged when several values were reported.

TABLE IV

AIBN-INITIATED POLYMERIZATION OF STYRENE AT 60°

Time, sec	[AIBN], M	$R_p \times 10^5$		$\bar{P}_n \times 10^{-3}$		$\bar{P}_w/\bar{P}_n$
		This work[a]	Ref 19b	This work	Ref 19b[b]	
5.46×10^4	4×10^{-5}	0.47		8.21		1.81
3.55×10^4	1×10^{-4}	0.73		7.05		1.74
2.52×10^4	2×10^{-4}	1.02		5.85		1.68
1.78×10^4	4×10^{-4}	1.44		4.67		1.62
1.07×10^4	1.1×10^{-3}	2.40		3.15		1.58
9.71×10^3	1.33×10^{-3}	2.65		2.91		1.57
5.92×10^3	3.59×10^{-3}	4.36	4.60	1.84	1.64	1.55
3.95×10^3	8.09×10^{-3}	6.53	6.95	1.23	1.18	1.54
3.22×10^3	1.23×10^{-2}	8.01		0.989		1.55
2.98×10^3	1.44×10^{-2}	8.66	9.43	0.912	0.846	1.56
2.39×10^3	2.25×10^{-2}	10.8	11.8	0.719	0.664	1.56
2.00×10^3	3.24×10^{-2}	12.9	14.0	0.589	0.552	1.57
1.52×10^3	5.76×10^{-2}	17.0	18.2	0.427	0.413	1.59
1.26×10^3	8.55×10^{-2}	20.5	20.6	0.340	0.340	1.62
1.07×10^3	1.20×10^{-1}	24.1	24.6	0.279	0.275	1.63
9.72×10^2	1.49×10^{-1}	26.5	26.7	0.246	0.242	1.64
9.15×10^2	1.70×10^{-1}	28.2	27.9	0.226	0.227	1.65

[a] All runs made to 3% conversion. [b] Calculated from eq III of ref 20.

TABLE V

SOURCE OF CHAIN ENDS IN THE POLYMERIZATION OF STYRENE INITIATED BY BENZOYL PEROXIDE AT 60°
CALCULATED FROM COMPUTER DATA

$[Bz_2O_2]$, M	10^5R_p	$(1/\bar{P}_n) \times 10^5$					
		Termination	C_M	$C_{AH}[AH]/[M]$	$C_I[I]/[M]$	PRT	Total
1×10^{-4}	0.41	4.90	0.69	6.23	0.1	0	11.9
1.25×10^{-4}	0.46	5.40	0.69	6.20	0.1	0	12.4
2.5×10^{-4}	0.63	7.47	0.69	6.09	0.15	0	14.4
5×10^{-4}	0.88	10.5	0.69	5.89	0.18	0	17.3
1×10^{-3}	1.24	14.9	0.69	5.66	0.64	0.03	21.8
2.5×10^{-3}	1.97	23.4	0.69	5.11	1.61	0.05	30.8
5×10^{-3}	2.79	33.2	0.69	4.59	3.26	0.09	41.8
1×10^{-2}	3.95	47.0	0.69	3.96	6.57	0.19	58.4
2×10^{-2}	5.59	66.6	0.69	3.27	13.2	0.40	84.1
4×10^{-2}	7.93	94.0	0.69	2.60	26.5	0.82	124.6
8×10^{-2}	11.2	132.8	0.69	2.03	53.0	1.72	190.4
1×10^{-1}	12.5	148.5	0.69	1.87	66.3	2.2	219.5
1.6×10^{-1}	15.8	187.6	0.69	1.54	106.2	3.7	299.4

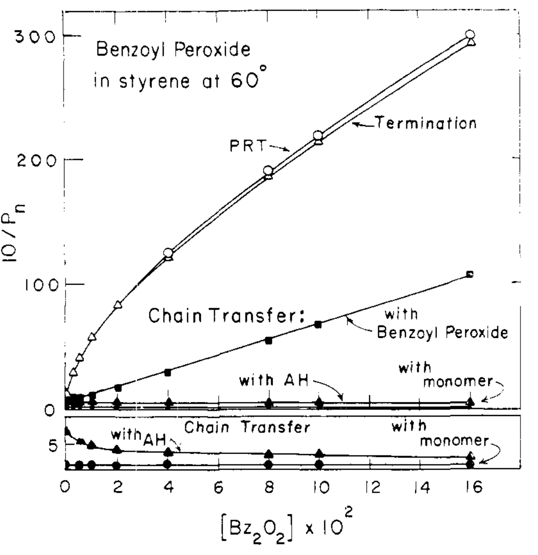

Figure 2. Sources of chain ends in the polymerization of styrene initiated by benzoyl peroxide at 60°. Insert shows the sources of chain ends for chain transfer with AH and monomer on an expanded scale. Data taken from Table III.

Table V gives the computer determined chain-end contributions for benzoyl peroxide-initiated polymerization calculated according to eq 10 and Figure 2 shows these sources of chain ends graphically. [Our Table V is similar to that published by Pryor and Fiske (Table V of ref 19a) and Figure 2 is similar to that originally published by Mayo, Gregg, and Matheson (Figure 7 of ref 20).] Table VI and Figure 3 give the same data for the AIBN-initiated polymerization.

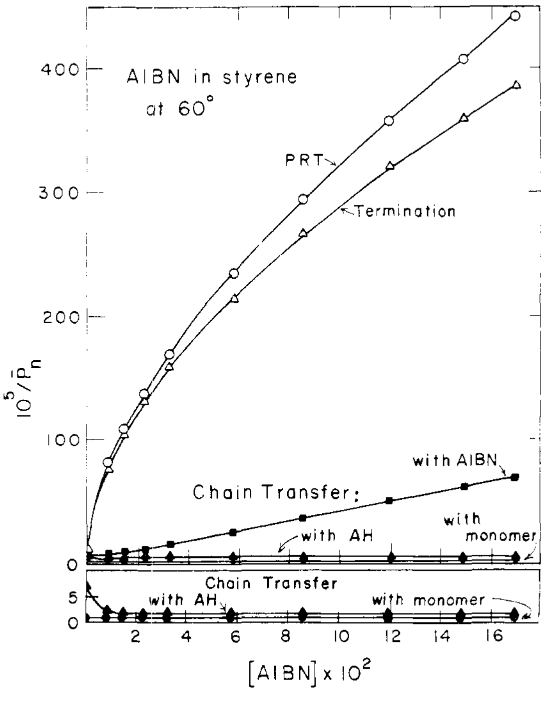

Figure 3. Sources of chain ends in the polymerization of styrene initiated by AIBN at 60°. Insert shows the sources of chain ends for chain transfer with AH and monomer on an expanded scale. Data taken from Table IV.

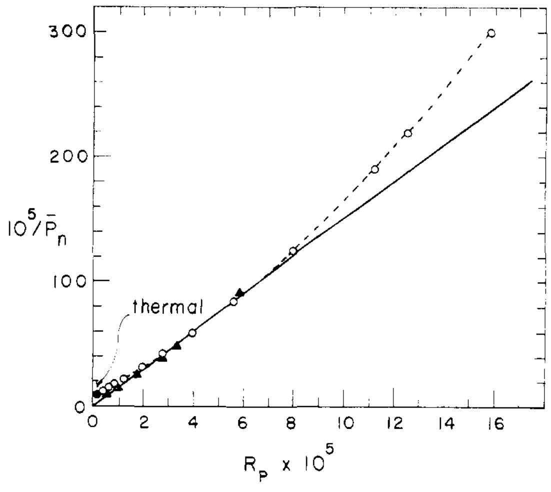

Figure 4. The polymerization of styrene initiated by benzoyl peroxide at 60°; 1/$\bar{P}_n$ *vs.* the rate of polymerization: circles, our data taken from Table V; triangles, data of Tobolsky.[31,33a]

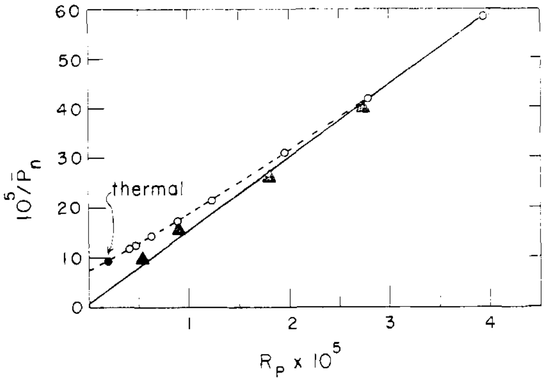

Figure 5. The polymerization of styrene initiated by benzoyl peroxide at 60°; an expansion of the lower portion of Figure 4.

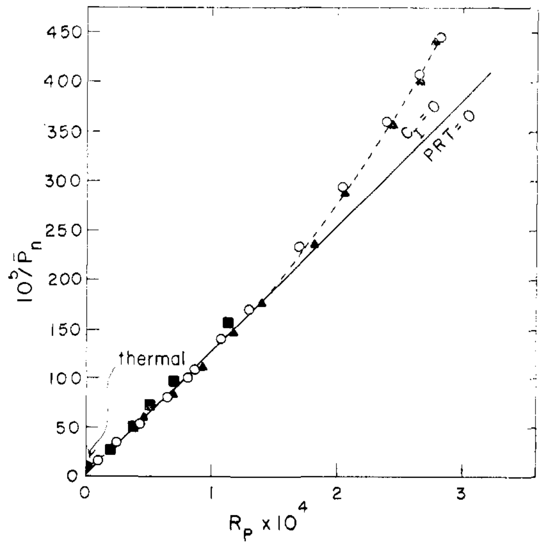

Figure 6. The polymerization of styrene initiated by AIBN at 60°; 1/$\bar{P}_n$ *vs.* the rate of polymerization: circles, our data taken from Table VI; squares, data of Tobolsky;[31,33a] triangles, data of Manabe, Utsumi, and Okamura.[19b]

TABLE VI
SOURCE OF CHAIN ENDS IN THE POLYMERIZATION OF STYRENE INITIATED BY AIBN AT 60°
CALCULATED FROM COMPUTER DATA

		$(1/\bar{P}_n) \times 10^5$					
[AIBN], *M*	$10^5 R_P$	Termination	C_M	$C_{AH}[AH]/[M]$	$C_I[I]/[M]$	*PRT*	Total
4×10^{-5}	0.47	5.32	0.69	6.16	0	0	12.2
1×10^{-4}	0.73	8.19	0.69	5.27	0	0	14.2
2×10^{-4}	1.02	11.5	0.69	4.70	0.11	0.09	17.1
4×10^{-4}	1.44	16.3	0.69	4.08	0.16	0.12	21.4
1.1×10^{-3}	2.40	27.2	0.69	3.09	0.44	0.35	31.8
1.33×10^{-3}	2.65	29.8	0.69	2.86	0.52	0.41	34.3
3.59×10^{-3}	4.36	48.9	0.69	2.02	1.44	1.12	54.3
8.09×10^{-3}	6.53	73.4	0.69	1.46	3.24	2.50	81.4
1.23×10^{-2}	8.01	90.0	0.69	1.20	4.9	3.8	101.1
1.44×10^{-2}	8.66	97.7	0.69	1.10	5.8	4.6	109.7
2.25×10^{-2}	10.8	121.3	0.69	0.95	9.1	7.1	139.1
3.24×10^{-2}	12.9	145.0	0.69	0.8	13.1	10.3	169.8
5.76×10^{-2}	17.0	191.1	0.69	0.6	23.3	18.4	234.1
8.55×10^{-2}	20.5	230.2	0.69	0.5	34.6	27.4	293.8
1.20×10^{-1}	24.1	270.0	0.69	0.4	48.4	38.6	358.5
1.49×10^{-1}	26.5	289.9	0.69	0.4	60.5	48.1	407.0
1.70×10^{-1}	28.2	317.5	0.69	0.3	69.0	55.0	441.9

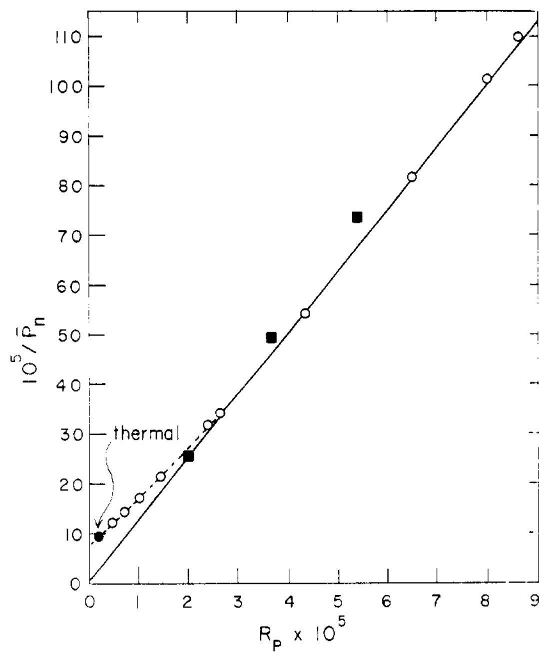

Figure 7. The polymerization of styrene initiated by AIBN at 60°; an expansion of the lower portion of Figure 6.

Tables V and VI and Figures 2 and 3 are in agreement with the published data except for the fraction of chain ends attributed to chain transfer to monomer and to AH. In these cases, we believe the computer data are correct. In our discussion on the assignment of rate constants to the thermal step, we attributed the observed amount of transfer to the sum of transfer by monomer and AH (eq 8). Our data agree with the experimental results which have polymerization times greater than 10 hr, the amount of time needed for AH to reach a steady-state concentration (Table I). The polymerization using higher initiator concentrations which involve reaction times of less than 10 hr should show a decrease in the contribution of transfer with AH to the chain end forming processes. This has not been previously observed since the method used by Mayo[20] for determining the monomer chain transfer constant is sensitive only at low peroxide concentrations where run times must be greater than 10 hr.

There has been some confusion in the literature over the sensitivity of a plot of $1/\bar{P}_n$ *vs.* R_P (eq 6) to transfer with AIBN and benzoyl peroxide. According to Tobolsky,[31,33a] such a plot appears to be similar for both benzoyl peroxide and AIBN and shows no curvature; from this he concludes that neither initiator undergoes transfer. Manabe, Utsumi, and Okamura[19b] showed that at higher AIBN concentrations this plot does show curvature which they attributed to primary radical termination. However, similar plots of our data for both benzoyl peroxide (Figures 4 and 5) and AIBN (Figures 6 and 7) show curvature at both low and high initiator concentrations. Since our study indicates that primary radical termination is unimportant in the benzoyl peroxide-initiated polymerization, the curvature at high initiator concentrations may result from chain transfer to initiator only. This implies that a similar curvature for AIBN could result from both chain transfer to initiator and primary radical termination as Pryor and Fiske[19a] have suggested. At the low initiator concentrations, the curvature is probably due to transfer with AH.

Experimental Section

REMECH was run on an IBM 360 computer. A copy of REMECH on magnetic tape is available from W. A. Benjamin;[18b] it is written for a CDC 6400 or IBM 7090 computer. Henry R. Streiffer, a programmer in the LSU Chemistry Department, converted the program to run on the IBM 360 computer.

The thermal polymerization was run using 300-sec intervals; polymerizations initiated by Bz_2O_2 and AIBN were run using the even increments method in REMECH with 0.5% conversion increments. We used a styrene concentration of 8.6 *M*.