Kinetics of Radical Polymerization of Vinyl Acetate Initiated by 1-Azobisphenylethane

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ABSTRACT: Vinyl acetate was polymerized using high concentrations of 1-azobisphenyl-ethane (APE) as the initiator. Its polymerization rate was 30 times slower than that initiated by 2,2'-azobisisobutyronitrile, although the production rates of primary radicals were the same for both initiators. Such a slow rate can be explained kinetically on the assumption that the rate constant (k_i) for the addition of phenylethyl radicals to the monomer is much smaller than the propagation rate constant (k_p), where $k_{ti}/k_i k_p = 6.07 \times 10^{-11} \exp(12500/T)$ dm^3 mol^{-1} s^{-1} (k_{ti}, primary radical termination rate constant and T, absolute temperature). The molecular weights of the polymers were controlled by the transfer of propagating radicals to APE where the transfer constant was estimated to be $C_{trC} = 31 \exp(-1860/T)$.

KEY WORDS   Vinyl Acetate / 1-Azobisphenylethane / Polymerization Rate / Molecular Weight / Kinetics / Primary Radical / Addition to Monomer / Termination / Transfer to Initiator /

1-Azobisphenylethane (APE) is an initiator for radical polymerizations[1] and thermally decomposes to yield 1-phenylethyl radicals (PER). The rate of cross termination in copolymerization between methacrylonitrile and styrene was compared with that of the bimolecular reaction between dimethylcyanomethylradicals and PER because of its similarity in structure (CH$_3$CHC$_6$H$_5$) to the end radical of polystyrene.[2] Further, the chain length dependence of the termination rate for the polymerization of styrene initiated by PER was analyzed on the assumption that PER is a radical with $n = 1$.[3,4]

In this article, the polymerization of vinyl acetate (VAc) in the presence of high concentration APE is reported. The rate was 30 times slower than that initiated by 2,2'-azobisisobutyronitrile (AIBN), although both the production rates of primary radicals were the same. Further, it was proportional to [M]$^{1.5 \sim 2}$, but independent of [APE]. These phenomena can be explained by assuming that the rate of addition to VAc is very slow compared with that of propagation. The molecular weight was approximately proportional to [M]/[APE] and independent of the polymerization rate. This indicates the molecular weight to be controlled by the transfer to APE. The radical produced by this transfer may be stable, and therefore will hardly adds to VAc.

THEORY

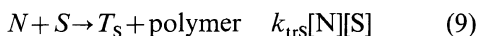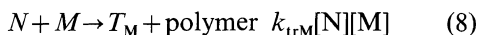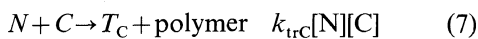Polymerization scheme is as follows:

Initiation:

$$C \rightarrow 2R \qquad\qquad 2fk_d[C] \qquad (1)$$

$$R + M \rightarrow N_1 \qquad\qquad k_i[R][M] \qquad (2)$$

Propagation:

$$N_n + M \rightarrow N_{n+1} \qquad\qquad k_p[N][M] \qquad (3)$$

Termination:

$$N + N \rightarrow \text{polymers} \qquad \bar{k}_t[N]^2 \qquad (4)$$

$$N + R \rightarrow \text{polymer} \qquad k_{ti}[N][R] \qquad (5)$$

$$T_C + N \rightarrow \text{polymer} \qquad k_{trt}[N][T_C] \qquad (6)$$

Transfer:

$$N + C \rightarrow T_C + \text{polymer} \quad k_{trC}[N][C] \qquad (7)$$

$$N + M \rightarrow T_M + \text{polymer} \; k_{trM}[N][M] \qquad (8)$$

$$N + S \rightarrow T_S + \text{polymer} \; k_{trS}[N][S] \qquad (9)$$

where T_M and T_S immediately add to monomers, but not T_C.

The polymerization rate can then be expressed as

$$R_p = k_p[M][N] + k_i[R][M] \qquad (10)$$

$$\simeq k_p[M][N] \qquad (11)$$

The material balance gives

$$\frac{d[R]}{dt} = 2fk_d[C] - k_i[R][M] - k_{ti}[R][N] = 0 \qquad (12)$$

$$\frac{d[N]}{dt} = k_i[R][M] - \bar{k}_t[N]^2$$

$$- k_{ti}[N][R] - k_{trC}[N][C]$$

$$- k_{trt}[T_C][N] = 0 \qquad (13)$$

$$\frac{d[T_C]}{dt} = k_{trC}[N][C] - k_{trt}[N][T_C] = 0 \qquad (14)$$

It is assumed that

$$k_{ti}[N][R] \gg \bar{k}_t[N]^2 \qquad (15)$$

This assumption was very useful for treating the polymerization rates of VAc initiated by AIBN,[5] and those of styrene and methylmethacrylate initiated by azobisdiphenylmethane[3] when [C] was high and [M] was low. Now, the concentration of polymer radical is shown as

$$[N] = \left(\frac{k_i[M]}{2k_{ti}} + \frac{fk_d}{2k_{trC}} \right)$$

$$\times \left\{ \left[1 + \frac{2fk_d[M]}{k_{ti}k_{trC} \left(\frac{k_i[M]}{k_{ti}} + \frac{fk_d}{k_{trC}} \right)^2} \right]^{1/2} - 1 \right\} \qquad (16)$$

$$\simeq \frac{k_i[M]/k_{ti}}{1 + (C_{trC}/fk_d)(k_ik_p/k_{ti})[M]} \qquad (17)$$

The latter was derived from the former, using a familiar approximation as $(1 + 2x)^{1/2} \simeq 1 + x - \cdots$. Accordingly, the relationship between [M] and R_p is

$$\frac{[M]^2}{R_p} \simeq \frac{k_{ti}}{k_ik_p} + \frac{C_{trC}}{fk_d}[M] \qquad (18)$$

For a very small value of [M], eq 18 becomes one already derived.[5] The relationship between various reactants and chain length is given by

$$\frac{k_p[M][N]}{\bar{n}} = k_{ti}[N][R] + k_{trt}[N][T_C]$$

$$+ k_{trC}[N][C] + k_{trC}[N][M]$$

$$+ k_{trS}[N][S] \qquad (19)$$

Using eq 12, 13, and 14, eq 19 is rewritten as

$$\frac{1}{\bar{n}} - C_{trM} - C_{trS}\frac{[S]}{[M]} = 2C_{trC}\frac{[C]}{[M]}$$

$$+ \frac{(2fk_d[C])k_{ti}/k_ik_p[M]^2}{1 + k_{ti}R_p/k_ik_p[M]^2} \qquad (20)$$

EXPERIMENTAL

Commercial VAc and AIBN were purified by methods described in earlier papers.[6,7] APE was prepared as described before.[1] Mixtures of VAc, an initiator, and ethyl acetate as the polymerization solvent were placed in an ampoule and degassed at about 10^{-3} mmHg by the freeze-thaw technique. The molecular weight of polymers produced was rather small, as shown in Table I, and the weight loss on the purification of the polymers was thus not negligible. Further, the separation of APE from the polymers could not be carried out satisfactorily. Accordingly, the conversions were estimated by gel permeation chromatography (GPC). Ultimate conversions were less than 5%. To calculate the M_n and M_w of poly(VAc), the GPC calibration curve for polystyrene was modified

Table I. Polymerization of VAc initiated by APE

Temp	[C]	[M]	$10^6 R_p$	M_n	M_w	M_w/M_n	$2C_{trC}$
°C	mol dm^{-3}	mol dm^{-3}	mol dm^{-3} s^{-1}				
53	0.20	5.18	5.76	11830	23100	1.95	0.18
	0.20	1.727	0.851				
	0.20	0.576	0.115				
60	0.04	10.15	25.4	64350	129800	1.99	
	0.10	10.05	30.8				
	0.20	9.72	31.9	22800	43910	1.92	0.18
	0.20	4.08	9.19	8890	18830	2.12	0.19
	0.20	2.72	4.13	5600	12100	2.18	0.20
	0.20	1.82	2.23	4080	8270	2.03	0.18
	0.20	1.21	1.10	2590	5230	2.02	0.19
	0.20	0.807	0.506				
70	0.10	9.78	99.2	30800	60100	1.95	0.25
	0.10	4.89	35.3	14970	30400	2.03	0.25
	0.10	2.45	11.7	7410	15340	2.07	0.26
	0.10	1.22	4.16	3980	8280	2.08	0.23
	0.10	0.612	0.966				
80	0.10	9.64	333	27600	56700	2.05	0.28
	0.10	4.82	113	15700	29900	1.90	0.23
	0.10	2.41	35.2	7080	14540	2.05	0.23
	0.10	1.21	10.0	3590	6720	1.87	0.25
	0.10	0.612	2.50				
90	0.10	9.49	1098	23500	47800	2.03	0.32
	0.10	4.74	324	11460	24600	2.15	0.32
	0.10	2.37	96.2	6320	12040	1.91	0.29
	0.10	1.19	29.1	2670	5680	2.12	0.34
	0.10	0.593	4.40				

using $[\eta] = 1.98 \times 10^{-4} \ M_v^{0.695}$ at $n \geq 60$ and $[\eta] = 1.05 \times 10^{-3} \ M_v^{0.50}$ at $n < 60$ in tetrahydrofuran at 38°C. These equations were obtained using

$$[\eta] = K M_v^a \qquad (21)$$

$$\frac{[\eta] M_w}{K_s} = \left\{ \sum_{j=1}^{\infty} w_j M_{js}^{[a(1+a_s)/(1+a)]} \right\}$$

$$\left\{ \sum_{j=1}^{\infty} w_j M_{js}^{[(1+a_s)/(1+a)]} \right\} \qquad (22)$$

Equation 22 was derived by replacing M_n in Mahabadi and O'Driscoll's equation[8] with M_w, and M_w was determined by the light scattering method.

RESULTS AND DISCUSSION

The kinetic data obtained are shown in Table I. The polymerization rate was 3.19×10^{-5} mol dm^{-3} s^{-1} for the bulk polymerization initiated by APE at 60°C and [C] = 0.200 mol dm^{-3}. With AIBN as the initiator, the rate was 106×10^{-5} mol dm^{-3} s^{-1} at [C] = 0.00647 mol dm^{-3}. Even though $2fk_d[C] = 3.26 \times 10^{-8}$ mol dm^{-3} s^{-1} in both the above cases, the polymerization rate initiated by APE was 30 times slower than that initiated by AIBN, where $fk_d = 1.63 \times 10^{-7}$ s^{-1} for APE and 5.04×10^{-6} for AIBN.[2] For [APE] ≥ 0.1 mol dm^{-3}, the polymerization rate was proportional to $[M]^{1.8 \pm 0.1}$ at 53°C, $[M]^{1.6 \pm 0.1}$ at 60°C, $[M]^{1.7 \pm 0.1}$ at 70°C, $[M]^{1.8 \pm 0.1}$ at 80°C,
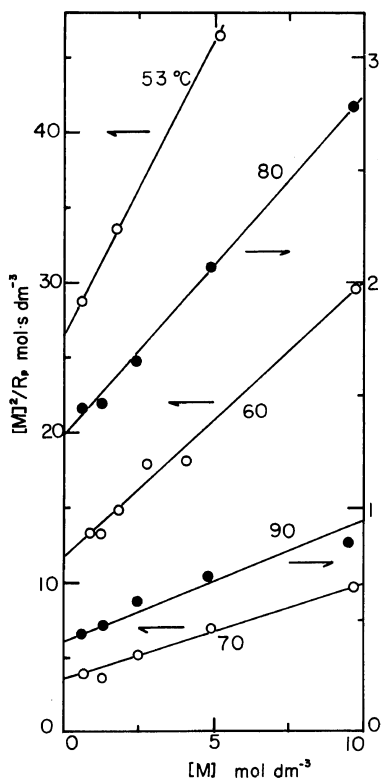
Figure 1. Analysis of polymerization rates by eq 19.

Table II. Some values calculated for the polymerization of VA initiated by APE

Temp	$k_{ti}/10^4 k_i k_p$	$\lambda C_{trC}/10^4 fk_d$	C_{trC}	f
°C	dm³ mol⁻¹ s⁻¹	s		
53	277	196	0.09	0.50
60	120	90	0.10	0.40
70	36	30	0.12	0.37
80	12.7	7.90	0.13	0.37
90	4.1	2.25	0.16	0.46
				(mean = 0.42)

and $[M]^{1.9 \pm 0.1}$ at 90°C; it should be independent of [APE] (Table I). Thus, the data should be analyzed by eq 18. The values of $k_{ti}/k_i k_p$ and C_{trC}/fk_d were estimated from the intercept and the slope (Figure 1) and are shown in Table II. The Arrhenius equations are applicable to these values (Figures 2 and 3), which are then written as
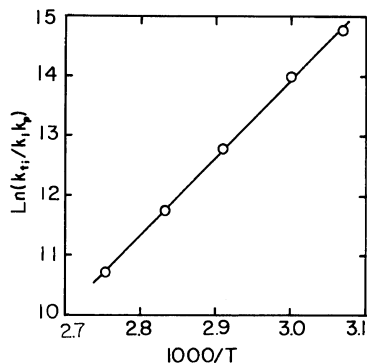

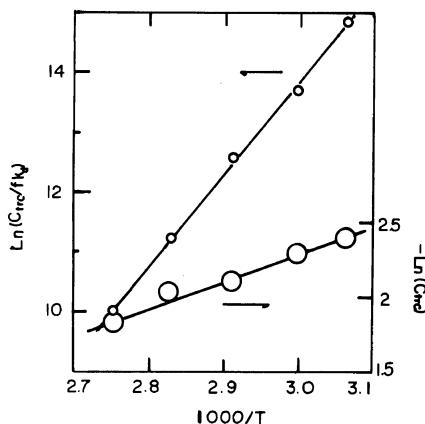**Figure 2.** Relationship between $k_{ti}/k_i k_p$ and T.

Figure 3. Relationships among C_{trC}, fk_d, and T.

$$\frac{k_{ti}}{k_i k_p} = 6.07 \times 10^{-11} \exp\left(\frac{24800}{RT}\right)$$
$$\text{dm}^3 \text{ s mol}^{-1} \quad (23)$$

$$\frac{C_{trC}}{fk_d} = 5.3 \times 10^{-14} \exp\left(\frac{29300}{RT}\right) \quad \text{s} \quad (24)$$

The value of k_i may be estimated by the relation[2,5,7]

$$k_i \simeq k_{ST:VAc} = k_{ST:ST} \cdot \left(\frac{k_{ST:VAc}}{k_{ST:ST}}\right) \quad (25)$$

At 60°C, k_i was found to be 3.0 dm³ mol⁻¹ s⁻¹ with $k_{ST:ST} = 164$ dm³ mol⁻¹ s⁻¹ and $k_{ST:ST}/k_{ST:VAc} = 55$.[9,10] The values of $k_{VAc:VAc}$ obtained before were very much scatter.[10] Because such a scattering was in the range of $k_p = 670 \sim 19000$ dm³ mol⁻¹ s⁻¹,[10] $k_i \ll k_p$ in the

present polymerization should be completely satisfied.

The above discussion is greatly dependent on the assumption as inequality 15 and thus is examined as follows. Inequality 17 is rewritten as

$$\frac{k_p^2}{k_t} \cdot \frac{k_{ti}}{k_i k_p} \gg \frac{R_p}{2 f k_d [C]} \left(1 + \frac{k_{ti}}{k_i k_p} \cdot \frac{R_p}{[M]^2} \right) \quad (26)$$

The left term was calculated to be 100000 at 60°C, where $k_p^2/k_t = 0.126$ dm^{3}mol^{-1}s^{-1},[9] $k_p = 1980$ dm^{3}mol^{-1}s^{-1},[9] $k_i \simeq k_{ST:VAc} = 3.0$ dm^{3}mol^{-1}s^{-1}, and $k_{ti} = 4 \times 10^9$ dm^{3}mol^{-1}s^{-1} as a diffusion-controlled rate constant.[11] The right term was smaller than 1000, where $2 f k_d [C] = 4.8 \times 10^{-8}$ was used.[2] It is apparent that the right term is negligibly smaller than that on the left; thus, inequality 15 is satisfied. In conclusion, under the present conditions, the data cannot be treated by an ordinary equation such as $R_p \propto [C]^{1/2}[M]$. If $k_p = 1980$ dm^{3}mol^{-1}s^{-1} at 60°C is used,[9] the value of k_{ti} becomes 5.9×10^9 dm^{3}mol^{-1}s^{-1}. This rate constant is quite reasonable in view of the diffusion-controlled theory.[11] Here, $k_p = 1980$ and was calculated from the most probable Arrhenius equation. This shows that a reasonable value of k_{ti} can be calculated.

In order to use eq 20, C_{trM} and C_{trS} must be calculated by[12]

$$C_{trM} = 0.0347 \exp(-3450/RT)$$

$$C_{trS} = 0.0351 \exp(-3170/RT)$$

The ratio ($=2C_{trC}$) of ($1/\bar{n} - C_{trM} - C_{trS}[S]/[M]$) to $[C]/[M]$ should be constant at a given temperature (Table I). Thus, the first term on the right of eq 20 is not comparable to the second term. Because $1/\bar{n}$ is considerably larger than ($C_{trM} + C_{trS}[S]/[M]$), the chain length of the polymer produced is controlled by the transfer to APE. The average values of C_{trC} obtained at given temperatures are shown in Table II. The transfer constant C_{trC} may also be treated by the following Arrhenius equation (Figure 3) as

$$C_{trC} = 31 \exp\left(-\frac{3700}{RT}\right) \quad (27)$$

Equations 24 and 27 give an activation energy of 33.0 kcal mol^{-1} for $f k_d$. This value is in a very good agreement with the 32.6 kcal mol^{-1} in an equation such as[1]

$$k_d = 6.43 \times 10^{14} \exp(-32600/RT) \quad (28)$$

The value of f can be calculated from those obtained for $C_{trC}/f k_d$ and C_{trC}, and eq 28, as shown in Table II and may be independent of temperature ($f \simeq 0.42$).

The values of C_{trC} are much larger than those of usual azo initiators.[10] Perhaps, this is due to the fact that APE has two methenyl hydrogens as $C_6H_5\underline{C}H(CH_3)N=N-$ which may be easily abstracted by polyVAc radicals. This is reasonable since the value of $C_{trC}/2 = 0.05$ (C_{trC} is divided by 2 because of two methenyl hydrogens) at 60°C is comparable with $C_{trS} = 0.07$ for triphenylmethane[13] whose methenyl hydrogen can be abstracted to yield triphenylmethyl radicals. Therefore, the transfer reaction may be shown as

$$N + HCCH_3C_6H_5N = NC_6H_5CH_3CH \rightarrow$$

$$HCCH_3C_6H_5N = NC_6H_5CH_3C\cdot$$
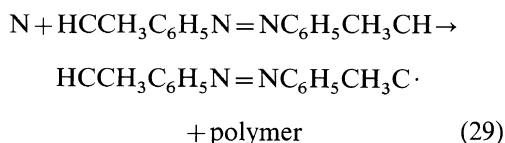
$$+ \text{polymer} \quad (29)$$

The stability of this radical is higher than that of PER and comparable with that of the triphenylmethyl radical, which hardly adds to monomers and inhibits polymerization.[14] Accordingly, the APE radical does not add to VAc and reacts only with polyVAc radicals. Consequently, the polymerization rate is further decreased by the transfer (29).

NOMENCLATURE

R_p	= polymerization rate
$\bar{n}$	= chain length (number-average degree of polymerization)
[C]	= initiator concentration
[M]	= monomer concentration
[S]	= solvent concentration

[R]	=	primary radical concentration
[N]	=	polymer radical concentration
$[T_A]$	=	small radical produced by transfer to A ($=C$, M, S)
f	=	fraction of primary radical escaping from the solvent cage
k_d	=	initiator decomposition rate constant
k_p	=	propagation rate constant
k_i	=	rate constant for addition of R to M
k_{ti}	=	rate constant for the primary radical termination between N and R
k_{trt}	=	rate constant of termination between T_C and N
$\bar{k}_t$	=	rate constant of termination between N and N
k_{trA}	=	rate constant of transfer to A ($C_{trA} = k_{trA}/k_p$)
$k_{A:B}$	=	rate constant of propagation of radical A to monomer B
T	=	absolute temperature
R	=	gas constant
w_j	=	weight fraction of jth species in a polymer
M_j	=	molecular weight of jth species in a polymer
M_{js}	=	molecular weight of jth species in polystyrene
$[\eta]$	=	intrinsic viscosity
K, a	=	Mark–Houwink constants for a polymer
K_s, a_s	=	Mark–Houwink constants for a polystyrene standard
M_n	=	number-average molecular weight ($=1/\sum w_j/M_j$)
M_w	=	weight-average molecular weight ($=\sum w_j M_j$)
M_v	=	viscosity-average molecular weight $[=(\sum w_j M_j{}^a)^{1/a}]$
n	=	degree of polymerization

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