Kinetics of Free-Radical Polymerization of Vinylidene Chloride in Homogeneous *N*-Methylpyrrolidone Solution

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ABSTRACT: Thermal and photochemical free-radical polymerization rates for vinylidene chloride in homogeneous *N*-methylpyrrolidone solution were measured dilatometrically in the temperature range 25 to 75 °C. The results are summarized by the expressions $\log (k_p/k_t^{1/2}) = 2.96 - 1390T^{-1}$ and $\log (k_p/k_t) = -3.0 - 810T^{-1}$, where k_p and k_t are the second-order propagation and termination rate constants in units of dm^3 mol^{-1} s^{-1}. The corresponding activation energies are $E_p = 9 \pm 1.4$ kcal mol^{-1} and $E_t = 5 \pm 2.5$ kcal mol^{-1}, both considerably smaller than earlier published figures for heterogeneous conditions. Chain transfer constants to monomer and solvent are also reported.

The free-radical polymerization of vinylidene chloride in *n*-hexane solution was long ago studied by Burnett and Melville.[1] Applying the standard photochemical rotating-sector technique, they measured radical lifetimes and deduced apparent bimolecular rate constants for chain growth and chain termination at several temperatures. Anomalously high activation energies were found: $E_p = 25$ kcal mol^{-1} for propagation and $E_t = 40$ kcal mol^{-1} for termination. The corresponding frequency factors were also very high, about 10^{16} dm^3 mol^{-1} s^{-1} for propagation and 10^{30} dm^3 mol^{-1} s^{-1} for termination.

Burnett and Melville clearly recognized that these unusual figures were related to the fact that the polymer was highly insoluble in the monomer–solvent mixtures employed and therefore precipitated (presumably in semicrystalline form) virtually at the start of every kinetic experiment. The complicated nature of the polymerization process in such heterogeneous systems, involving the trapping of growing radicals, has been emphasized and elaborated by many workers, especially by Bamford, Jenkins, and collaborators.[2–4] Nevertheless, the Burnett–Melville rate parameters given above have been listed without comment in a recent standard compilation.[5] It might be added that several more recent kinetic studies of vinylidene chloride polymerzation[6] also were conducted in heterogeneous systems and thus gave no direct information on the problem of the anomalous rate constants.

We now report the kinetics of thermal and photochemical vinylidene chloride polymerization in homogeneous liquid phase, with *N*-methylpyrrolidone as solvent, AIBN as thermal initiator, and biacetyl as photoinitiator. This investigation was possible only after the relatively recent discovery by Wessling[7] of several good solvents for the polymer. As might have been anticipated, our measurements lead to activation energies and frequency factors in the normal range expected for free-radical polymerizations of olefinic monomers. In a short companion paper[8] we also describe the kinetics of vinyl chloride–vinylidene chloride copolymerization in homogeneous *N*-methylpyrrolidone solution.

Experimental Section

(a) Chemicals. Vinylidene chloride (Monomer-Polymer Laboratories) was distilled over anhydrous magnesium sulfate just before preparation of solutions for kinetic experiments. The solvent, *N*-methyl-2 pyrrolidone (Eastman Kodak), after drying over anhydrous potassium carbonate and anhydrous ceric sulfate, was purified by vacuum distillation through a 50 cm Vigreux column (67.0 °C (4 mm)). The initiator, AIBN (2,2-azobisisobutyronitrile), was recrystallized twice from 95% ethanol. The photoinitiator, biacetyl (2,3-butanedione, Fisher), was used as received. Inhibitors included 1,1-diphenyl-2-picrylhydrazyl (DPPH, Aldrich), cupric chloride dihydrate (J. T. Baker), anhydrous cupric chloride (prepared from the dihydrate by simple heating under N$_2$), and duroquinone (an ancient gift from Dr. Harold Kwart).

(b) Procedures. Rates of polymerization were followed in a double-capillary dilatometer (bore radius ca. 0.5 mm) permitting easy filling and removal of bubbles. The volume of the dilatometer (ca. 10 cm^3) was calibrated with mercury over the range of temperatures employed. Polymerization rates were calculated from the relation

$$R_p = -(\Delta V/\Delta t) V_0^{-1}(\bar{V}_m - \bar{V}_p)^{-1}$$

where V_0 is the initial volume of solution and $(\bar{V}_m - \bar{V}_p)$ is the difference in partial molar volume between monomer (m) and polymer (p) in the solvent. This quantity, which varies with temperature, was evaluated from measured densities of monomer solutions and polymer solutions in *N*-methylpyrrolidone at three different temperatures.

Before a run, three freeze–pump–thaw cycles with liquid nitrogen were carried out and the dilatometer was then sealed while evacuated. The dilatometer was placed in a water bath regulated to ±0.02 °C and the change of solution level in the capillaries was observed with a Gaertner Scientific Co. cathetometer. Darkening of the solutions during kinetic measurements was negligible.

For the photopolymerization studies the arrangement for intermittent illumination was modeled after that used by Kwart, Broadbent, and Bartlett.[9] The light source, a 500 W Xenon lamp (Hanovia Division, Englehard Industries, Inc.), was kindly loaned by Dr. C. L. Braun of this department. A rotating disk with a dark-to-light period ratio of 2.00 ± 0.02 was constructed and used to interrupt the collimated light beam at various frequencies. Known relative incident light intensities were obtained by means of calibrated screens.

(c) Molecular Weight Determinations. Polymers were precipitated by pouring into methanol and were then dried to constant weight under vacuum at room temperature followed by a final short period at 40 °C. Intrinsic viscosities in *N*-methylpyrrolidone were determined at 25 °C and used to calculate viscosity-average molecular weights with the aid of the Mark-Houwink relation recently established in this laboratory:[10]

$$[\eta] = 1.31 \times 10^{-4} M_v^{0.69} \text{ dL g}^{-1} \quad (1)$$

These were converted to number-average molecular weights by means of the formula[11]

$$(M_v/M_n)^a = \Gamma(1 + a + b)/b^a\Gamma(1 + b) \quad (2)$$

with $a = 0.69$ and b equal either to 2 (giving $M_v/M_n = 1.43$, and corresponding to combination of all radical pairs in the termination step) or to unity (giving $M_v/M_n = 1.86$, and corresponding to disproportionation).

Results and Discussion

Thermal Polymerization. Reactions were followed to only about 1% conversion, so that all the reported polymerization rates can be regarded as initial values. Results for the thermal (dark) reaction at 60 °C are given in Table I for a number of concentrations of monomer and AIBN initiator. At a given monomer concentration, the polymerization rate R_p is quite closely proportional to $[I]^{1/2}$, but its dependence on monomer concentration exceeds first order. As Figure 1 shows, the effective order in monomer is about 1.27 at 60 °C. Such devia-

Table I
Thermal Polymerization Rates at 60 °C

$[M]^a$	$[I]^b \times 10^2$	$R_p{}^c \times 10^5$	$[M]$	$[I] \times 10^2$	$R_p \times 10^5$
0.707	1.91	1.30	4.70	1.93	11.7
0.936	1.91	1.63	1.10	0.954	1.43
1.19	1.92	1.93	1.46	0.957	1.96
1.29	1.92	2.30	1.86	0.955	3.02
1.45	1.92	2.94	2.68	0.955	4.58
2.30	1.92	5.54	4.03	0.962	7.38
2.96	1.92	7.58	1.46	3.86	4.24
3.55	1.93	9.12	1.45	0.484	1.52

[a] Vinylidene chloride concentration, mol dm^{-3}. [b] AIBN concentration, mol dm^{-3}. [c] Polymerization rate, mol dm^{-3} s^{-1}.

Table II
Inhibition by $CuCl_2$ at 60 °C ($[M] = 2.02$ mol dm^{-3}; $[I] = 9.68 \times 10^{-3}$ mol dm^{-3})

$[CuCl_2] \times 10^4$, mol dm^{-3}	$t_i{}^a$	$2k_d[I]t_i/[CuCl_2]$
2.82	25	1.06
3.77	34	1.08
5.86	52	1.06
7.24	64	1.06

[a] Induction period (min).

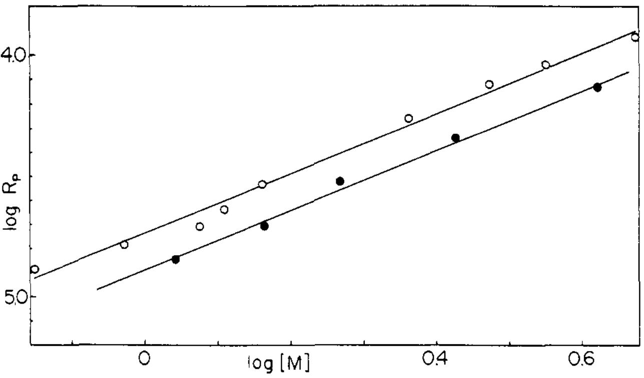

Figure 1. log–log plot of polymerization rate against monomer concentration at 60 °C. Open circles, $[I] = 1.92 \times 10^{-2}$ M; filled circles, $[I] = 0.96 \times 10^{-2}$ M.

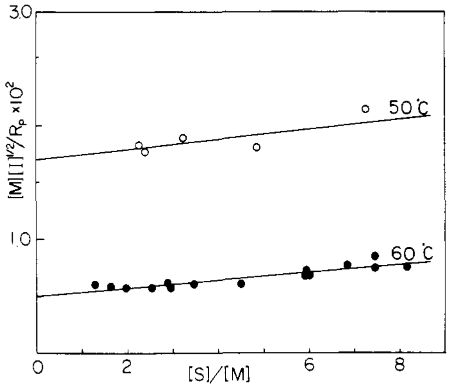

Figure 2. Rates of thermal polymerization plotted according to eq 7.

tions from first-order kinetics are common for polymerizations in solution and can be rationalized in several alternative ways, such as a cage effect[12,13] or low initiation efficiency accompanied by high primary-radical reactivity in chain termination.[14,15] The latter explanation would require some departure from the observed proportionality of R_p to $[I]^{1/2}$, while the former seems unlikely in view of our results with inhibitors, as described below. As explained later, we prefer to rationalize our results in terms of chain transfer to solvent and moderate reactivity of the resulting solvent radicals.

Four different materials were tried as inhibitors. In order of increasing effectiveness, these were duroquinone, cupric chloride dihydrate, diphenylpicrylhydrazyl (DPPH), and anhydrous $CuCl_2$. The first three behaved as retarders in varying degree, but the last gave quite sharp induction periods, with results at 60 °C listed in Table II. The last column of the table, for which we used a tabulated value[16] at 60 °C of $k_d = 1.03 \times 10^{-5}$ s^{-1} for the unimolecular decomposition rate constant of AIBN, shows that each $CuCl_2$ molecule accounts for one radical, probably by the simple reaction

$$RCH_2CCl_2\cdot + CuCl_2\cdot \rightarrow RCH_2CCl_3 + CuCl$$

We conclude that the efficiency of initiation is essentially 100% in the present system.

Kinetic Scheme I is used, and requires little comment.

Scheme I

Initiation	$I \rightarrow 2R\cdot \rightarrow 2M\cdot$	$R_i = 2fk_d[I]$
Propagation	$M\cdot + M \rightarrow M\cdot$	$R_p = k_p[M][M\cdot]$
Monomer transfer	$M\cdot + M \rightarrow P + M\cdot'$	$k_{trm}[M][M\cdot]$
Solvent transfer	$M\cdot + S \rightarrow P + S\cdot$	$k_{trs}[S][M\cdot]$
Regeneration	$M\cdot' + M \rightarrow M\cdot$	Very fast
	$S\cdot + M \rightarrow M\cdot$	$k_r[M][S\cdot]$
Termination	$M\cdot + M\cdot \rightarrow P$ or $2P$	$k_t[M\cdot]^2$
	$M\cdot + S\cdot \rightarrow P$	$\sigma k_t[M\cdot][S\cdot]$
	$S\cdot + S\cdot \rightarrow X$	$\sigma^2 k_t[S\cdot]^2$

We remark only that (a) we follow recent practice[5] in omitting an awkward and unnecessary factor of 2 in the definition of the termination rate, and that (b) the factor σ^2 in the defined rate of the last very minor termination step is assumed only for algebraic convenience but could be altered without appreciable effect on the numerical results. Steady-state balances in the radical species then give

$$2fk_d[I] + k_r[M][S\cdot] = k_t[M\cdot]^2 + \sigma k_t[S\cdot][M\cdot] + k_{trs}[S][M\cdot] \quad (3)$$

and

$$k_{trs}[S][M\cdot] = k_r[M][S\cdot] + \sigma k_t[M\cdot][S\cdot] + \sigma^2 k_t[S\cdot]^2 \quad (4)$$

The sum of the two equations leads to

$$[M\cdot] + \sigma[S\cdot] = (2fk_d[I]/k_t)^{1/2} \quad (5)$$

Now the observed proportionality of R_p to $[I]^{1/2}$ means that in this (or any other) scheme regeneration has to be highly efficient. We therefore neglect the last two (termination) terms on the right side of eq 4 and obtain

$$[S\cdot]/[M\cdot] = (k_{trs}/k_r)[S]/[M] \quad (6)$$

which permits elimination of $[S\cdot]$ from eq 5. The polymerization rate is then finally found to be

$$R_p \equiv k_p[M][M\cdot] = k_p[M](2fk_d[I]/K_t)^{1/2}/(1 + B[S]/[M]) \quad (7)$$

with the definition of a dimensionless ratio,

$$B \equiv \sigma k_{trs}/k_r \quad (8)$$

A test of eq 7 for the rate is shown in Figure 2 for the data of Table I; a plot of $[M][I]^{1/2}/R_p$ against $[S]/[M]$ gives a fair straight line. From the values of slope and intercept we obtain the figures $B = 6.2 \times 10^{-2}$ and $k_p(2fk_d/k_t)^{1/2} = 1.95 \times 10^{-4}$ dm$^{3/2}$ mol$^{-1/2}$ s^{-1} at 60 °C.

Rate measurements were also made at other temperatures and are given in Table III. At 40 and 50 °C the data are sufficiently numerous to indicate apparent reaction orders with respect to monomer; they give orders of 1.04 and 1.18 at these two temperatures, respectively. The corresponding values of B, obtained as

Table III
Thermal Polymerization Rates at Several Temperatures (units as in Table I)

Temp, °C	[M]	[I] × 10^2	R_p × 10^5	Temp, °C	[M]	[I] × 10^2	R_p × 10^5
75	1.427	0.944	7.11	50	3.02	1.02	1.77
70	1.431	0.95	4.62	50	3.07	1.02	1.76
65	1.455	0.96	2.82	45	2.26	1.04	0.83
55	2.27	1.04	2.02	45	2.71	1.04	1.07
55	1.82	1.04	1.67	40	4.14	1.02	0.89
55	2.24	0.98	1.97	40	4.94	1.02	1.05
55	1.46	0.97	1.15	40	3.05	1.02	0.59
50	1.22	1.02	0.58	40	2.00	1.02	0.42
50	1.73	1.01	0.97	35	2.27	1.04	0.30
50	2.44	1.01	1.30	35	2.72	1.04	0.38
				25	3.21	1.05	0.130

Table IV
Chain Transfer Experiments

Temp, °C	[M]	[S]/[M]	[I] × 10^2	$[\eta]$[a]	M_n[b] × 10^{-3}	$\left(\frac{1}{\bar{P}_n} - \frac{1}{2\nu}\right) \times 10^3$
50	1.32	6.66	1.97	0.070	4.8	16.4
	1.57	5.47	0.977	0.081	6.0	14.0
	1.86	4.49	0.99	0.095	7.5	11.0
	2.35	3.38	0.488	0.106	8.8	10.0
	3.67	1.87	1.53	0.151	14.7	5.4
	4.19	1.54	1.04	0.150	14.6	5.8
60	1.29	7.21	1.90	0.062	4.1	17.9
	1.86	4.46	0.96	0.082	6.1	13.0
	4.03	1.74	0.96	0.127	11.4	7.1
	4.70	1.37	1.90	0.139	13.1	5.8

[a] Intrinsic viscosity (dL g^{-1}) in *N*-methylpyrrolidone, 25 °C. [b] Calculated with eq 1 and 2, assuming combination of radicals.

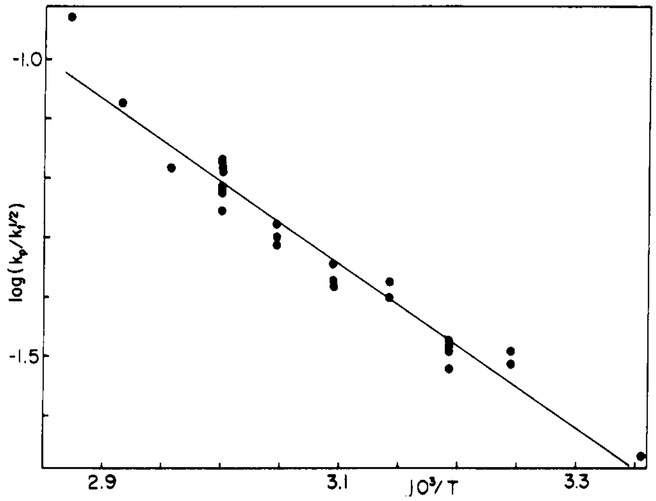

Figure 3. Arrhenius plot of $k_p/k_t^{1/2}$.

in Figure 3, are 2.0 × 10^{-2} at 40 °C and 3.6 × 10^{-2} at 50 °C. These figures are correlated by the equation

$$\log B = 6.42 - 2540T^{-1} \qquad (9)$$

but we do not attach great significance to the numerical parameters. We now use this relation, together with the data of Tables I and III and the assumption $f = 1$, to find values of $k_p/k_t^{1/2}$ at each temperature. In these calculations we used the expression

$$\log k_d = 15.93 - 6968T^{-1} \qquad (10)$$

for the frequently measured and tabulated first-order rate constant (in s^{-1}) of AIBN decomposition.[16] The results of these calculations are shown as an Arrhenius plot in Figure 3. The least-squares line through the points is given by

$$\log (k_p/k_t^{1/2}) = 2.96 - 1390T^{-1} \qquad (11)$$

with standard deviations of 0.10 and 40 K in intercept and slope, respectively. The figures would not be very different if we had elected to attribute the deviations from first-order kinetics in monomer to different secondary reactions; for example, if we use standard cage-effect kinetics[12,13] and plot $[M]^2[I]R_p^{-2}$ against $[M]^{-1}$, we obtain $k_p(2k_d/k_t)^{1/2} = 1.89 \times 10^{-4}$ dm$^{3/2}$ mol$^{-1/2}$ s^{-1} as compared to 1.95 × 10^{-4} from Figure 2.

Chain transfer was studied in the usual way by measuring solution viscosities of isolated low-conversion polymers. The standard relation is

$$1/\bar{P}_n = (b\nu)^{-1} + C_m + C_s[S][M]^{-1} \qquad (12)$$

where $\bar{P}_n$ is the number-average degree of polymerization and ν is the kinetic chain length, here given by

$$\nu = R_p/R_t = R_p/R_i$$
$$= k_p[M]/(2fk_d[I]k_t)^{1/2}(1 + B[S][M]^{-1}) \qquad (13)$$

The transfer constants have the usual definitions, $C_m = k_{trm}/k_p$ and $C_s = k_{trs}/k_p$, and the factor b is 2 for combination of radicals or unity for disproportionation. Transfer to initiator has been neglected.

The chain transfer data are given in Table IV and a plot is shown in Figure 4, both on the basis of combination of radicals (b = 2). Fortunately there is some compensation if the other choice (b = 1) is made, as the first two terms of eq 12 both are changed in the same direction. As presented, our measurements lead to 10^3C_m = 2.2 and 3.8 at 50 and 60 °C, respectively, while 10^3C_s = 2.0 at both temperatures. The latter figure allows some further speculation regarding the regeneration rate. With the value B = 6.2 × 10^{-2}, we have at 60 °C.

$$k_r/\sigma k_p = C_s/B = 3.2 \times 10^{-2} \qquad (14)$$

Assuming values of σ not too much different from unity, we thus conclude that the solvent radicals produced by transfer to *N*-methylpyrrolidone are only a few percent as efficient as growing chains in adding to vinylidene chloride monomer.

It was suggested to us by Professor Bartlett[17] that vinylidene chloride might exhibit spontaneous thermal polymerization[18] at temperatures in our experimental range. We were indeed able to

Table V
Photochemical Polymerization at Several Temperatures[a]

Temp, °C	[M]	[S]/[M]	$(R_p)_s \times 10^5$	τ_s, s	$(k_p/k_t)^b \times 10^6$
25	1.98	4.16	1.99	0.18 ± 0.02	1.8 ± 0.2
35	2.00	4.12	2.84	0.15 ± 0.02	2.2 ± 0.3
45	2.04	4.01	4.48	0.11 ± 0.02	2.7 ± 0.5
55	2.00	4.12	5.50	0.10 ± 0.03	3.2 ± 1.0

[a] Biacetyl (0.02 M) served as photoinitiator. [b] Calculated with eq 15.

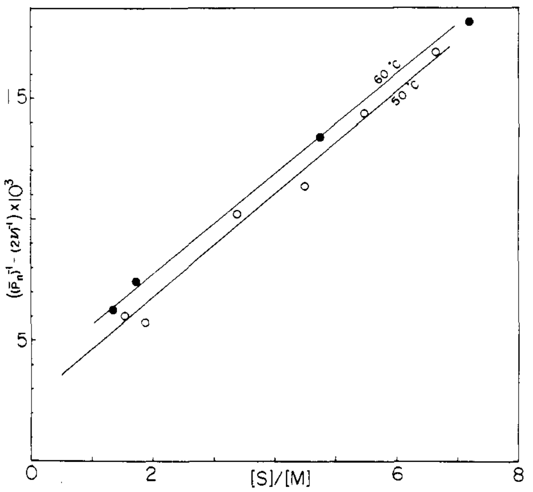

Figure 4. Chain transfer data at two temperatures. Intercepts give transfer constant to monomer, C_m; slopes give transfer constant to solvent, C_s.

observe some contraction in the dilatometer of monomer–solvent mixtures containing no added initiator. For example, at 65 °C we obtain $R_p \simeq 5.2 \times 10^{-6}$ mol dm^{-3} s^{-1} for [M] = 3.15 mol dm^{-3}. The rates at lower temperatures were considerably smaller and harder to reproduce, so we do not report any definitive spontaneous polymerization rates. It should be remarked that the correction for spontaneous polymerization required in the AIBN-initiated experiments is in all cases negligible.

Photopolymerization. The biacetyl photoinitiator concentration was about 0.020 mol dm^{-3}, which with our apparatus produced polymerization rates $(R_p)_s$ under steady illumination of the order of 2 to 6 × 10^{-5} mol dm^{-3} s^{-1}, quite similar in magnitude to those of the thermal polymerization experiments. Insertion of neutral filters showed proportionality of $(R_p)_s$ to the square root of the incident light intensity, as expected for sufficiently low light absorption. Typical results for the rotating-sector measurements are shown in Figure 5, where for two temperatures the observed ratios of $(R_p)_s$ to the average rates $\bar{R}_p$ under interrupted irradiation are plotted against the logarithm of the length t of an illumination period. The conditions and numerically derived quantities are given in Table V. The functional dependence of $(R_p)_s/\bar{R}_p$ on t is well known[9,13,19] and need not be written out here. The mean radical lifetime τ_s under steady illumination is given by

$$\tau_s = [\mathrm{M}\cdot]/R_t = [\mathrm{M}\cdot]/(k_t[\mathrm{M}\cdot]^2 + \sigma k_t[\mathrm{M}\cdot][\mathrm{S}\cdot] = k_p[\mathrm{M}]/k_t(R_p)_s(1 + B[\mathrm{S}][\mathrm{M}]^{-1}) \quad (15)$$

and thus the ratio k_p/k_t can be evaluated, with the results also given in Table V. They are reproduced by the relation

$$\log (k_p/k_t) = -3.0 - 810T^{-1} \quad (16)$$

but the uncertainties in these figures are quite large (cf. Table V), amounting to ±1.0 in the intercept and ±300 K in the slope. These rather large numbers are due to the relatively low accuracy of determining the lifetime τ_s.

Absolute Rate Constants. From eq 11 and 16 the individual rate constants are obtainable. We find for the propagation step

$$\log k_p = 9.0 - 1970T^{-1} \quad (17)$$

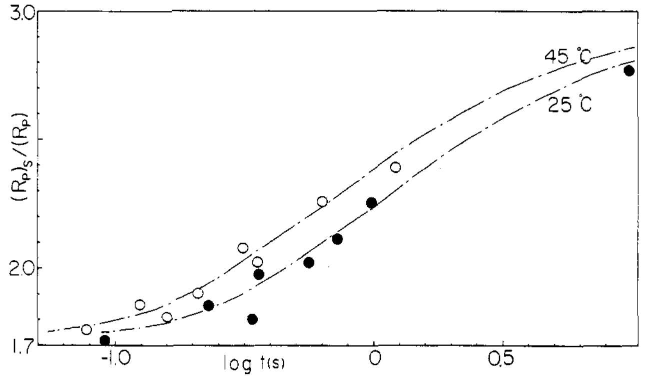

Figure 5. Interrupted photopolymerizations at two temperatures. Ratio of rates for steady and interrupted illumination as a function of illumination period.

with uncertainties of 1.0 and 300 K in the constants. The corresponding frequency factor is $A_p = 1 \times 10^9$ dm^3 mol^{-1} s^{-1}, and the activation energy is $E_p = 9.0 \pm 1.4$ kcal mol^{-1} = 38 ± 6 kJ mol^{-1}. Also, for termination,

$$\log k_t = 12.0 - 1160T^{-1} \quad (18)$$

with uncertainties of 2.0 and 600 K. Thus the frequency factor, $A_t = 1 \times 10^{12}$ dm^3 mol^{-1} s^{-1}, may be uncertain by a factor of 10^2 and the activation energy is $E_t = 5 \pm 2.5$ kcal mol^{-1} = 21 ± 12 kJ mol^{-1}. As remarked earlier, the above figures are quite different from those reported[1] for heterogeneous conditions, and in fact are quite normal among those[5] for other simple homogeneous free-radical polymerization systems.

Since the termination rate is diffusion controlled and k_t is therefore inversely proportional to solvent viscosity,[13] it should be mentioned that we measured the viscosity of N-methylpyrrolidone to be about 1.95 cP at 20 °C and 1.13 cP at 50 °C.

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Copolymerization Kinetics of Vinyl Chloride and Vinylidene Chloride in *N*-Methylpyrrolidone Solution

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ABSTRACT: Rates of vinyl chloride–vinylidene chloride copolymerization initiated by AIBN in homogeneous *N*-methylpyrrolidone solution were measured dilatometrically at 50 °C. The minimum in rate at intermediate compositions is far shallower than for systems in which the copolymer precipitates on formation. The results indicate that the rate constant for the termination step does not vary greatly with composition.

In the foregoing paper[1] the kinetics of thermal and photochemical free-radical polymerization of vinylidene chloride (VDC) in homogeneous *N*-methylpyrrolidone solution were reported. It was found that the rate constants and their temperature coefficients were quite normal, in contradistinction to earlier results obtained in heterogeneous systems. Here we describe some copolymerization rate measurements in the same solvent at 50 °C for mixtures of VDC with vinyl chloride (VC).

The VDC–VC copolymerization is of course of considerable practical importance, and has therefore received much attention.[2] Reactivity ratios have been measured several times.[3,4] Rate studies have been published for bulk copolymerization at 45 °C by Reinhardt[5] and at 47 °C by Bengough and Norrish[6] and for both bulk and emulsion copolymerization at 40 °C by Staudinger.[7] The outstanding feature of all these results is the relatively slow rate at intermediate compositions as compared to the rates of homopolymerization of the separate monomers. As remarked by Melville and Valentine,[8] a large relative rate of termination between unlike radicals is required to account for the results. We find less extreme behavior in the homogeneous system.

Experimental Section

Vinylidene chloride, AIBN, and *N*-methylpyrrolidone were purified as before.[1] Vinyl chloride (Matheson Gas Products) was distilled from the tank into a calibrated glass tube and then transferred to the dilatometer,[1] which was immersed in liquid nitrogen. Rate measurements were made as for the homopolymerization of vinylidene chloride, all at 50 °C controlled to within 0.01 °C.

Results

To facilitate analysis, all the measurements of the rate were made as closely as possible at the same initial concentration of AIBN (0.010 mol dm^{-3}) and at the same initial total monomer concentration (2.88 mol dm^{-3}). As before, polymerization was observed to only about 1% conversion and thus the reported copolymerization rates R_p are initial values. The results are given in Table I and displayed graphically in Figure 1. They are again shown as relative rates (based on the homopolymerization of vinylidene chloride) in Figure 2 to permit comparison with the data of Reinhardt[5] and of Staudinger[7] in heterogeneous systems. The differences among these sets of observations emphasize the strong influence of phase conditions on the radical termination step in both homopolymerization and copolymerization.

Discussion

Two different procedures have been used to analyze the results. The classical method is based on the presumption that the reactivity of a radical in both propagation and termination depends only on the identity of the terminal monomer unit and leads to the familiar equation[9–11]

$$R_p \equiv -\mathrm{d}([\mathrm{M}_1] + [\mathrm{M}_2])/\mathrm{d}t = \frac{R_i^{1/2}(r_1[\mathrm{M}_1]^2 + 2[\mathrm{M}_1][\mathrm{M}_2] + r_2[\mathrm{M}_2]^2)}{(r_1^2\delta_1^2[\mathrm{M}_1]^2 + 2\phi r_1 r_2 \delta_1 \delta_2 [\mathrm{M}_1][\mathrm{M}_2] + r_2^2\delta_2^2[\mathrm{M}_2]^2)^{1/2}} \tag{1}$$

with $\delta_1 = k_{t11}^{1/2}/k_{p11}$, $\delta_2 = k_{t22}^{1/2}/k_{p22}$, $\phi = k_{t12}/(k_{t11}k_{t22})^{1/2}$. In these expressions, R_i is the rate of initiation, the monomer concentrations are $[\mathrm{M}_1]$ and $[\mathrm{M}_2]$, r_1 and r_2 are the usual reactivity ratios, and the k_{pij} and k_{tij} are propagation and termination rate constants.

For a series of experiments all conducted at a constant value of R_i and a constant value of $[\mathrm{M}_1] + [\mathrm{M}_2]$, the above relation may be rewritten as follows:

$$R_p = \frac{(r_1 f_1^2 + 2f_1 f_2 + r_2 f_2^2)}{(r_1^2 f_1^2 R_{p1}^{-2} + 2\phi r_1 r_2 f_1 f_2 R_{p1}^{-1} R_{p2}^{-1} + r_2^2 f_2^2 R_{p2}^{-2})^{1/2}} \tag{2}$$

where we have put $f_2 = 1 - f_1 = [\mathrm{M}_2]/[\mathrm{M}]$, with $[\mathrm{M}] \equiv [\mathrm{M}_1] + [\mathrm{M}_2]$, and where R_{p1}, R_{p2} represent the rates of homopolymerization at the given values of R_i and $[\mathrm{M}]$, namely

$$R_1 = R_i^{1/2}[\mathrm{M}]/\delta_1, \qquad R_{p2} = R_i^{1/2}[\mathrm{M}]/\delta_2 \tag{3}$$

Since our experiments were all made at constant values of R_i and of $[\mathrm{M}]$, and since the reactivity ratios for the system are well known, the only unknown parameter in eq 2 is the cross-termination rate ratio ϕ. It is well known that there are some implicit assumptions in eq 1 or eq 2, for example, that initiation efficiency and the influence of other possible secondary reactions are independent of composition, and that penultimate influences on reactivity[12] can be ignored.

In Figure 1 curves based on eq 2 are drawn for several constant values of ϕ. With VC as monomer 1 and VDC as monomer **2**, we use $r_1 = 0.22$ and $r_2 = 3.8$, these being chosen as a weighted consensus of the published values.[3,4] It is seen that the data in *N*-methylpyrrolidone solution are best reproduced if ϕ is about 2. This result is consistent with the argument of Melville and Valentine,[8] who obtained the expression