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Bulk Polymerization of Methyl Methacrylate

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Synopsis

This manuscript reports on an experimental investigation of the chemical-initiated (AIBN) bulk polymerization of methyl methacrylate to limiting conversion at temperatures of 50°, 70°, and 90°C. The change in the cumulative differential molecular weight distribution (CDMWD) with respect to conversion was measured by gel permeation chromatography (GPC). These CDMWD's were differentiated to determine the instantaneous differential molecular weight distribution (instantaneous DMWD) over the range of conversions investigated. These experimental instantaneous DMWD's were found to agree with theoretical distributions predicted by classical free-radical kinetics over the entire conversion range and where diffusion control of the termination reactions is dramatic. A correlation of the dimensionless group α (where $\alpha = k_{td}R_p/k_p^2M^2$) with free volume is proposed. This correlation appears to adequately account for diffusion control of the termination reaction. A kinetic model for the bulk polymerization of methyl methacrylate has been developed. This model should find use in the design, simulation, and optimization of PMMA reactors.

MODEL DEVELOPMENT

Further detail of the material to be discussed here may be found elsewhere.[1] The reactions which are significant in the bulk polymerization of MMA with a free radical initiator follow.

Initiation:

I = rate of formation of free radicals of chain length unity, $R_1^{\cdot}$.

In order to keep the model as general as possible at this stage, we shall not consider the detailed mechanism of initiation, but rather will use the net production of radicals $R_1^{\cdot}$ in the analysis.

Propagation:

$$R_r^{\cdot} + M \xrightarrow{k_{pi}} R_{r+1}^{\cdot} \text{ (isotactic placement)}$$

$$R_r^{\cdot} + M \xrightarrow{k_{ps}} R_{r+1}^{\cdot} \text{ (syndiotactic placement)}$$

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Transfer:

$$R_r^{\cdot} + M \xrightarrow{k_{fm}} P_r + R_1$$

$$R_r^{\cdot} + C \xrightarrow{k_{fc}} P_r + R_1$$

Termination:

$$R_r^{\cdot} + R_s^{\cdot} \xrightarrow{k_{tc}} P_{r+s} \text{ (combination)}$$

$$R_r^{\cdot} + R_s^{\cdot} \xrightarrow{k_{td}} P_r + P_s \text{ (disproportionation)}$$

If we make the stationary-state hypothesis for free radicals, and neglect chain length dependence of the rate constants and consumption of monomer in reactions other than propagation, the following relationships may be derived:

$$\frac{dP_r}{dt} = R_p \left\{(\tau)(\tau + \beta) + \left(\frac{1}{2}\beta\right)(\tau + \beta)^2 r\right\} \phi^r \tag{1}$$

$$R_p = \frac{I}{\alpha + \beta} \tag{2}$$

$$r_N^{-1} = \tau + \beta/2 \tag{3}$$

$$\frac{r_w}{r_N} = 2\left\{1 - \left(\frac{\beta/2}{\tau + \beta}\right)^2\right\} \tag{4}$$

$$W_r = \{(\tau)(\tau + \beta) + (1/2\,\beta)(\tau + \beta)^2 r\} r\phi^r \tag{5a}$$

$$= \{(\tau)(\tau + \beta) + (1/2\,\beta)(\tau + \beta)^2 r\} r \exp(-(\tau + \beta)r) \tag{5b}$$

Equations (1) to (5) are for instantaneous values, where

$$\alpha = \frac{k_{td}}{k_p^2}\frac{R_p}{M^2} = \frac{k_{td}}{k_p^2}\frac{\left\{-\frac{1}{V}\frac{dMV}{dt}\right\}}{\left(\frac{M_0(1 - X)}{(1 + \epsilon X)}\right)^2} = \frac{k_{td}}{k_p^2}\frac{1}{M_0}\frac{dX}{dt}\frac{(1 + \epsilon X)}{(1 - X)^2}$$

$$\beta = \frac{k_{tc}}{k_p^2}\frac{R_p}{M^2}$$

$$C_m = \frac{k_{fm}}{k_p}$$

$$C_c = \frac{k_{fc}C}{k_pM}$$

$$\tau = \alpha + C_m + C_c$$

$$\phi = \left\{\frac{1}{1 + \tau + \beta}\right\}$$

The cumulative differential chain length distribution may be found from the instantaneous distribution as

$$(W_r)_{\text{cumulative}} = \frac{\int_0^X W_r(X)dX}{X} \tag{6}$$

where X the conversion is given by

$$X = \frac{M_0V_0 - MV}{M_0V_0} \tag{7}$$

and M_0 = initial monomer concentration, M = monomer concentration at conversion X, V_0 = initial volume of the polymerizing mixture, V = volume of polymerizing mixture at conversion X, and ϵ is defined in eq. (11).

For the bulk polymerization of MMA using AIBN, it was found that $\tau \gg \beta$ and $\alpha \gg C_m + C_c$.

In addition, molecular weight measurements by GPC indicated that transfer to polymer and terminal double bond polymerization were at most of minor importance. These points will be considered more fully later in the discussion of experimental results.

Equations which are used to interpret our experimental data follow:

Rate of Polymerization

Before the Gel Effect

$$\frac{R_p}{C_0^{1/2}} = K_1M \tag{8}$$

$$X = 1 - \exp(-K_1C_0^{1/2}t) \tag{9}$$

$$V_f = 0.025 + \alpha_m(T - T_{gm}) + \{\alpha_p(T - T_{gp}) - \alpha_m(T - T_{gm})\}\phi_p \tag{10}$$

with

$$K_1 = \sqrt{(2fk_d/k_{td})k_p^2}$$

$$\phi_p = \frac{X(1 + \epsilon)}{1 + \epsilon X}$$

where ϵ is defined using the linear contraction equation

$$V = V_0(1 + \epsilon X). \tag{11}$$

Horie[2] showed that limiting conversions in MMA polymerization occur at the glass transition temperature. He employed equations based on the "Free Volume Theory." Two important relationships involve the effect of molecular weight of a polymer on its glass transition temperature (T_{gp}) derived by Fox and Flory,[3] where

$$T_{gp} = T_{g\infty} - \frac{2\rho N\theta}{\alpha_p M_v} \tag{12}$$

and $T_{g\infty}$ is the glass transition temperature of the polymer with infinite molecular weight, ρ is the polymer density, N is Avogadro's number, α_p is the difference between the volume expansion coefficient of the polymer in the melt and in the glassy state, θ is the contribution of the chain end to the free volume, M_v is the viscosity average molecular weight, T_g is the glass transition temperature of the polymer monomer mixture derived by Kelly and Bueche,[3] and is defined as

$$T_g = \frac{\{\alpha_p\phi_p T_{gp} + \alpha_m(1 - \phi_p)T_{gm}\}}{\{\alpha_p\phi_p + \alpha_m(1 - \phi_p)\}} \tag{13a}$$

and ϕ is the volume fraction in the system, with subscript p indicating polymer and m, monomer.

Horie recommends the following values for the MMA–PMMA system: $\rho = 1.1$ g/cm^3, $\theta = 80$ Å,[3] $\alpha_p = 0.48 \times 10^{-3}$/°C, $T_{g\infty} = 114$ °C, $T_{gm} = -106$ °C, and $\alpha_m = 1.0 \times 10^{-3}$/°C.

The equation for T_g was obtained assuming the additivity of free volume of monomer and polymer:

$$\begin{aligned} V_f &= V_{fp}\phi_p + V_{fm}\phi_m \\ &= [0.025 + \alpha_p(T - T_{gp})]\phi_p + [0.025 + \alpha_m(T - T_{gm})]\phi_m. \end{aligned} \tag{13b}$$

At the glass transition temperature, $T = T_g$ and $V_f = 0.025$, and eq. (13b) reduces to eq. (13a). Horie set T_g in eq. (13a) equal to the polymerization temperature and, using his measured M_v, estimated T_{gp} from eq. (12). He then solved eq. (13a) for ϕ_p. This limiting ϕ_p was found to agree with limiting ϕ_p found from his polymerizations. Horie did not examine the decrease in free volume during the polymerization as we did. For the large molecular weights observed in our polymerizations of MMA, the effect of molecular weight on T_{gp} is small and can be neglected.

During the Gel Effect

$$\frac{dX}{dt} = Kk_p(X - b)(a - X) \tag{14}$$

$$X = \frac{[a \exp\{(a - b)(Kk_p t + C)\} + b]}{[1 + \exp\{(a - b)(Kk_p t + C)\}]} \tag{15}$$

Equations (14) and (15) were derived by Sawada.[11] K, a, b, and C are empirical constants.

Limiting Conversion

$$\frac{dX}{dt} = 0 \tag{16}$$

$$V_f = 0.025 \tag{17}$$

$$\phi_p = \frac{-\alpha_m(T - T_{gm})}{[\alpha_p(T - T_{gp}) - \alpha_m(T - T_{gm})]} \tag{18}$$

$$X = \left\{\frac{\phi_p}{1 + \epsilon(1 - \phi_p)}\right\} \tag{19}$$

Molecular Weight Distribution

For all conversions,

$$W_r = \alpha^2 r \phi^r \equiv \alpha^2 r \exp(-\alpha r) \tag{20}$$

$$r_N^{-1} = \alpha \tag{21}$$

$$\frac{r_w}{r_N} = 2 \tag{22}$$

$$(W_r)_{\text{cumulative}} = \frac{r \int_0^X \alpha^2 \phi^r dX}{X} \tag{23}$$

with

$$\phi = \frac{1}{1 + \alpha}.$$

Before the Gel Effect

$$\alpha = \alpha_1 \frac{1 + \epsilon X}{(1 - X)^2} \tag{24}$$

with

$$\alpha_1 = \frac{k_{td}}{k_p^2} \frac{1}{M_0} \frac{dX}{dt}.$$

During the Gel Effect

$$\alpha_1 = f(X). \tag{25}$$

This dependence of α_1 on conversion is a result of the dependence of both (k_{td}/k_p^2) and R_p on conversion. If diffusion control were absent at all conversions, (k_{td}/k_p^2) would not depend on conversion. The parameter α_1 was determined experimentally using GPC chromatograms, and two new methods of data reduction were developed in this investigation. These are "The Method of Differential Chromatograms" and "The Method of Chromatogram Heights." In previous kinetic studies, GPC was used to obtain M_n and M_w from which kinetic parameters such as k_t/k_p^2 were determined.[4,5] May[6] used GPC chromatogram heights but was hindered by the relatively unrefined state of both GPC technology and numerical techniques.

The Method of Chromatogram Heights. This method involves fitting the heights of a normalized experimental cumulative DMWD with a theoretical DMWD such as eq. (23) where in general the parameter α is a function of conversion. When using GPC chromatograms, it is ad-

vantageous to use heights centered about the peak and in the vicinity of the points of inflection. There are two reasons for the choice of these particular heights. The first is due to the fact that the central heights are much more reproducible than heights on the high and low molecular weight ends of the chromatograms. Reproducibility studies have confirmed this fact. Secondly, axial dispersion in GPC lowers the peak height and broadens the chromatogram. The heights which are least affected by axial dispersion are those near the points of inflection. The use of heights near the points of inflection reduces ones reliance on methods of correcting GPC chromatograms for axial dispersion. Often when dealing with broad chromatograms, it is found that resolution at the high molecular weight end is poor. These chromatogram heights are not reliable, and M_w calculated therefrom may be significantly in error. Heights at the low molecular weight end of the chromatogram can be influenced by low molecular weight impurities and additionally by the fact that refractive index can vary with molecular weight. Unless special precautions are taken, heights at the low molecular weight end of the chromatogram can be in error, and M_n calculated therefrom may be significantly in error.

In this investigation a three-variable search for $(C_m + C_c)$, α_1, and β_1 in eq. (6) at low conversions was used. It was found that $\alpha_1 \gg (C_m + C_c)$ and β_1. Fitting GPC chromatograms at high conversions, therefore, involved a search for the variation of the single parameter α_1 with conversion. The choice of a suitable function for this variation was greatly assisted by the method which now follows.

The Method of Differential Chromatograms. This method also uses GPC chromatogram heights. The chromatograms used in the search are instantaneous and are calculated by subtracting chromatograms found at different polymerization times. A best α_1 in the theoretical distribution. eq. (20) is found by fitting this experimental instantaneous DMWD. This involves a single-variable search. Because we measured DMWD's at quite large intervals of conversion, we expected very approximate α_1 values over the conversion range, but sufficiently accurate to permit the determination of a suitable functional form for use with the "Method of Chromatogram Heights" and to show that experimental instantaneous DMWD's could be predicted by classical free-radical kinetics. For this polymerization, experimental distributions were in agreement with eq. (20) even though the cumulative DMWD's were bimodal.

EXPERIMENTAL

The initiator, AIBN (Eastman Organic Chemicals), was recrystallized twice and sometimes three times from absolute methanol. The methyl methacrylate was purchased from Rohm and Haas and contained 10 ppm monomethyl ether of hydroquinone (MEHQ). This inhibitor was removed by distillation under reduced pressure with sulfur to eliminate polymerization in the reboiler. A 4-ft glass column packed with glass cylinders

and a high reflux ratio gave adequate separation. The distillate was tested by nitrosation of the hydroquinone. Comparison was made with an undistilled sample. Absence of any brown coloration indicated removal of the inhibitor. A number of GPC runs which included injection of monomer indicated no high molecular weight impurities in the monomer.

Polymerizations were conducted in degassed glass ampoules of various surface-to-volume ratios (see Fig. 1). Shrinkage data were obtained by following the decrease in the level of the reacting mixture. Conversion was determined by dissolving a known weight of the reaction mixture in

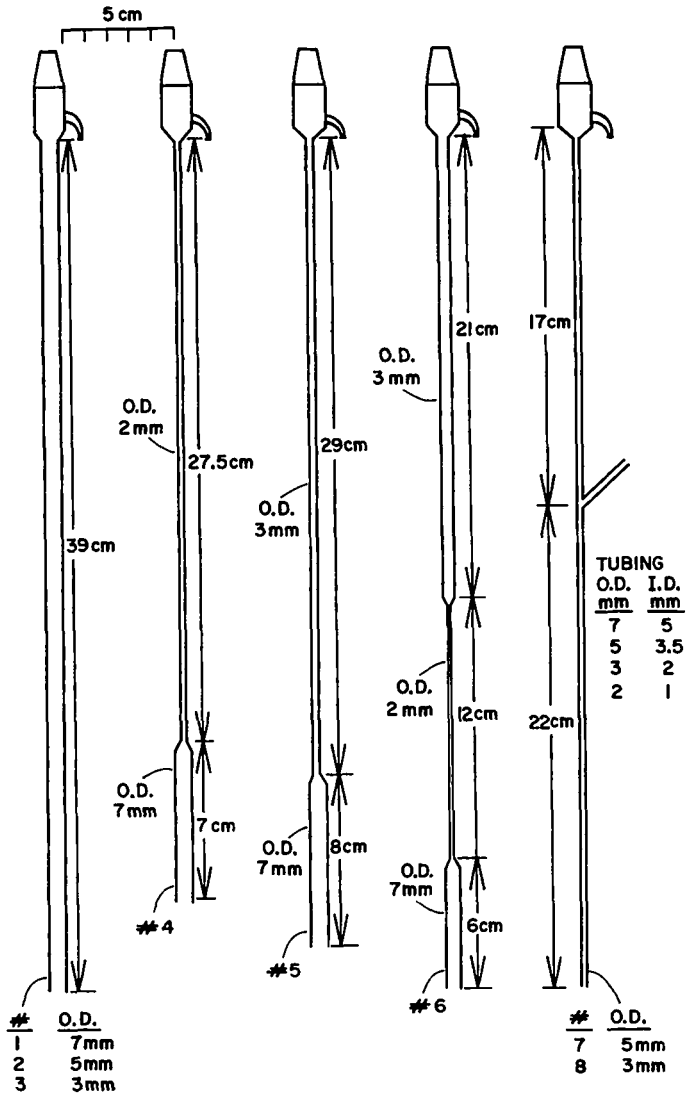

Fig. 1. Ampoule reactors.

TABLE I
Summary of Polymerization Conditions[a]

Temperature, °C	AIBN, wt-%
50	0.3
	0.391
	0.5
70	0.3
	0.5
90	0
	0.3
	0.5

[a] All polymerizations except those for thermal were continued to limiting conversion.

acetone, adding MEHQ as inhibitor, later precipitating the polymer in a 20-fold excess of methanol drying the precipitate at 50°C under vacuum. An estimate of low molecular weight loss in this procedure was obtained by injecting the reacted monomer–polymer mixture directly into the GPC. Molecular weight distribution information was obtained by analyzing selected samples by GPC. A few polymer samples were analyzed for tacticity with a high-resolution NMR (220 MHz). Experimental details may be found elsewhere.[1] Polymerization conditions are summarized in Table I.

Several experiments and analyses were replicated or at least duplicated. Figure 2 shows the conversion-versus-time curves and the main replicates.

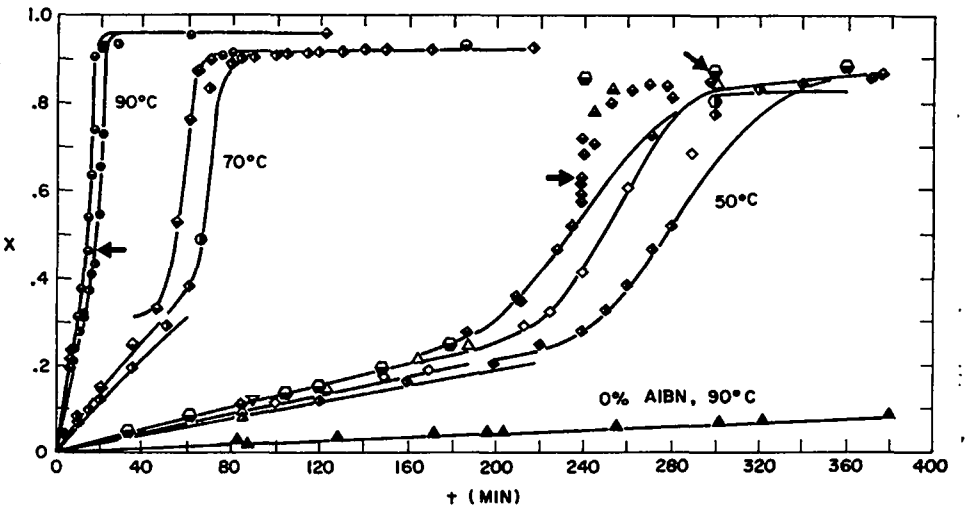

Fig. 2. Conversion vs. time at 50°, 70°, and 90°C: (◒) ampoule type 1; (▽) ampoule type 2; (△▲) ampoule type 2; (◆◇◆) ampoule type 3; (◑◒) ampoule type 6; (◒◆◒) .5% AIBN; (◇△) .4% AIBN; (◑◆) .3% AIBN; (▲) 0 wt. % AIBN; (—→) site of main replicates; (— —) model fit (first order at low conversion, Sawada equation at high conversion). Types 1 and 2 have 10 ppm MEHQ present as inhibitor.

TABLE II
Reproducibility Studies. Conversions by Gravimetric Method

Sample no.	Conversion
(1) PMMA Prepared at 50.0°C, 0.5 wt-% AIBN, Reaction Time = 300.0 min	
9I	.8529
7F	.8453
7G	.8491
9O	.8509
9U	.8552
1E	.8694
6B	.8525
9X	.8522
8C	.8548
9Z	.8501
9H	.8485
9E	.8474
7E	.8465
9N	.8518
7H	.8504
7I	.8541
Mean	.8519
Sample estimate of variance	3.00 E-05
.95 Confidence Limits	.0029
Confidence limits as per cent of mean	.34
(2) PMMA Prepared at 50.0°C, 0.5 wt-% AIBN, Reaction Time = 240.0 min	
9W	.6842
9Y	.6146
7C	.7161
10J	.6279
2N	.6179
8B	.6810
8D	.6828
9B	.5863
9G	.6739
9M	.6735
9V	.6843
9C	.5739
9D	.7070
7B	.7126
Mean	.6597
Sample estimate of variance	2.18 E-03
.95 Confidence Limits	.0270
Confidence limits as per cent of mean	4.08
(3) PMMA Prepared at 90.0°C, 0.5 wt-% AIBN, Reaction Time = 14.0 min.	
26D	.4603
26E	.4571
26G	.4587
26H	.4569
26I	.4582
Mean	.4582
Sample estimate of variance	1.843 E-06
.95 Confidence limits	.0017
Confidence limits as per cent of mean	.36

TABLE III
Reproducibility Studies. GPC Molecular Weight Averages

	Run	M_n	M_w	M_z	$M_{(z+1)}$	M_w/M_n
(1) Five Different Ampoule Experiments at the Onset of the Gel Effect Prepared at 90.0°C., 0.5 wt-% AIBN[a]						
	602	5.959E + 04	2.008E + 05	1.241E + 06	3.082E + 06	3.37
	603	5.723E + 04	2.017E + 05	1.490E + 06	3.982E + 06	3.52
	604	5.731E + 04	2.012E + 05	1.777E + 06	5.204E + 06	3.51
	605	5.525E + 04	1.468E + 05	1.035E + 06	4.659E + 06	2.66
	606	6.164E + 04	2.282E + 05	1.677E + 06	4.150E + 06	3.70
Mean		5.820E + 04	1.957E + 05	1.444E + 06	4.215E + 06	3.35
Sample estimate of variance		6.050E + 06	8.849E + 08	9.395E + 10	6.294E + 11	.164
.95 Confidence limits		3.054E + 03	3.693E + 04	3.805E + 05	9.849E + 05	.504
Confidence limits as a per cent of mean		5.246E + 00	1.887E + 01	2.635E + 01	2.336E + 01	15.2
(2) Six Different GPC Injections of the Same PMMA Sample Prepared at 70.0°C, 0.5 wt-% AIBN[a]						
	610	2.758E + 05	1.405E + 06	3.518E + 06	5.597E + 06	5.09
	615	2.552E + 05	1.381E + 06	3.441E + 06	5.367E + 06	5.41
	616	2.573E + 05	1.389E + 06	3.480E + 06	5.492E + 06	5.40
	617	2.597E + 05	1.365E + 06	3.371E + 06	5.204E + 06	5.25
	618	2.499E + 05	1.355E + 06	3.335E + 06	5.107E + 06	5.42
	619	2.632E + 05	1.392E + 06	3.472E + 06	5.434E + 06	5.29
Mean		2.602E + 05	1.381E + 06	3.436E + 06	5.367E + 06	5.31
Sample estimate of variance		7.842E + 07	3.386E + 08	4.881E + 09	3.344E + 10	.0162
.95 Confidence Limits		9.295E + 03	1.931E + 04	7.333E + 04	1.919E + 05	.1338
Confidence limits as a per cent of mean		3.572E + 00	1.398E + 00	2.134E + 00	3.576E + 00	2.52

[a] Reaction time 14.0 min, approximate conversion 45% (refer to Table II).
[b] Limiting conversion.

TABLE IV. Gravimetrically Determined and Predicted Conversions[a]

Sample no.	Ampoule type	Time, min	X Exp	X First order	X Sawada	Free volume
11S	2	60.0	.0626	.0622		.172
11R	2	84.6	.0852	.0866		.168
11T	3	120.0	.1152	.1205		.164
11Q	3	160.0	.1585	.1574		.157
11P	3	200.0	.2023	.1927	.2157	.150
11B	5	220.0	.2493	.2098	.2361	.143
11F	3	240.0	.2795		.2832	.138
11C	5	250.0	.3273		.3234	.130
11G	3	260.0	.3831		.3776	.121
11H	3	272.0	.4628		.4599	.106
11D	3	280.0	.5147		.5222	.097
11U	3	290.0	.6807		.6000	.065
11O	5	300.0	.7721		.6716	.046
11V	1	300.0	.8002		.6716	.040
11N	3	320.0	.8297		.7761	.034
11M	3	340.0	.8411		.8303	.031
11K	3	371.3	.8522		.8609	.029
11L	3	460.0	.8647		.8703	.026
11J	3	187.3 hr	.9240		.8704	.012

[a] Reaction temperature = 50.0°C: AIBN concn. = .3 wt-%: first-order rate constant = 1.070 E-03 (l./min); Sawada equation constants: A = .8704, B = .2020, KKP = 7.076E-02, C = −1.994E + 01.

TABLE V. Gravimetrically Determined and Predicted Conversion[a]

Sample no.	Ampoule type	Time, min	X Exp	X First order	X Sawada	Free volume
12A	2	60.0	.0709	.0704		.171
4I	2	84.6	.1036	.0978		.166
12B	2	100.0	.1095	.1145		.165
4H	2	124.2	.1449	.1402		.159
12D	3	150.0	.1671	.1668		.156
12E	3	170.0	.1889	.1868	.2100	.153
4G	2	187.5	.2433	.2039	.2222	.144
12F	3	212.8	.2871		.2752	.137
12R	3	225.0	.3221		.3303	.131
12Q	5	240.4	.4127		.4384	.115
4D	2	254.4	.5642		.5624	.088
12K	3	260.0	.5985		.6116	.081
12H	3	272.0	.7232		.7046	.056
12L	3	280.0	.8079		.7528	.038
4C	2	302.4	.8413		.8305	.031
4B	2	371.3	.8601		.8694	.027
12I	3	460.0	.8662		.8704	.025
4F	2	266.3 hr	.9170		.8704	.014

[a] Reaction temperature = 50.0°C; AIBN concn. = .391 wt-%; First order rate constant = 1.216E-03 (l./min); Sawada equation constants: A = .8704, B = .2020, KKP = 8.104E-02, C = −2.038 E + 01.

TABLE VI. Gravimetrically Determined and Predicted Conversions[a]

Sample no.	Ampoule type	Time, min	X Exp	X First order	X Sawada	Free volume
2A	1	33.0	.0433	.0452		.175
1A	1	60.0	.0810	.0807		.169
2B	1	60.0	.0758	.0807		.170
10A	2	60.0	.0801	.0807		.169
10Z	2	84.6	.1096	.1119		.165
10K	2	84.6	.1117	.1119		.164
2K	2	90.0	.1128	.1186		.164
2C	1	105.0	.1300	.1369		.162
1B	1	120.0	.1518	.1549		.158
2L	2	120.0	.1461	.1549		.159
6A	3	120.0	.1568	.1549		.158
9F	3	120.0	.1481	.1550		.159
2M	2	135.0	.1663	.1725		.156
2D	1	150.0	.1922	.1897	.2157	.152
8A	2	150.0	.1913	.1897	.2157	.152
2E	1	165.5	.2174	.2071	.2283	.148
2F	1	180.0	.2463	.2231	.2498	.143
1C	1	180.0	.2473	.2231	.2498	.143
10P	3	186.4	.2612		.2638	.141
6H	3	186.4	.2727		.2638	.139
10L	2	186.4	.2703		.2638	.140
10M	2	210.0	.3571		.3500	.125
10I	3	210.0	.3492		.3500	.126
6C	3	212.2	.3404		.3611	.128
10Q	3	228.3	.4601		.4603	.107
10T	3	235.0	.5165		.5080	.097
9W	2	240.0	.6842		.5443	.064
9Y	3	240.0	.6146		.5443	.078
7C	3	240.0	.7161		.5443	.058
10J	3	240.0	.6279		.5443	.075
2N	2	240.0	.6179		.5443	.077
8B	2	240.0	.6810		.5443	.065
8D	2	240.0	.6828		.5443	.064
9B	3	240.0	.5863		.5443	.083
1D	1	240.0	.8562		.5443	.028
9G	2	240.0	.6739		.5443	.066
9M	3	240.0	.6735		.5443	.066
9V	2	240.0	.6843		.5443	.064
9C	3	240.0	.5739		.5445	.086
9D	2	240.0	.7070		.5445	.060
7B	3	240.0	.7126		.5449	.058
7M	3	240.6	.6836		.5493	.064
10W	3	245.0	.7043		.5804	.060
10O	2	245.0	.7790		.5804	.044
10V	3	245.0	.7129		.5804	.058
10H	3	252.0	.7996		.6291	.040
10N	2	254.4	.8270		.6449	.034
6F	3	262.5	.8263		.6959	.034
2G	1	270.0	.8451		.7333	.030
9K	2	270.0	.8330		.7333	.033

TABLE VI (*continued*)

Sample no.	Ampoule type	Time, min	X Exp	X First order	X Sawada	Free volume
7J	3	270.0	.8403		.7333	.031
6G	3	278.3	.8415		.7686	.031
9I	2	300.0	.8529		.8267	.028
7F	3	300.0	.8453		.8267	.030
7G	3	300.0	.8491		.8267	.029
9O	3	300.0	.8509		.8267	.029
9U	3	300.0	.8552		.8267	.028
1E	1	300.0	.8694		.8267	.025
6B	3	300.0	.8525		.8267	.028
9X	2	300.0	.8522		.8267	.029
8C	2	300.0	.8548		.8267	.028
9Z	3	300.0	.8501		.8267	.029
9H	2	300.0	.8485		.8268	.029
9E	3	300.0	.8474		.8268	.030
7E	3	300.1	.8465		.8269	.030
9N	3	300.1	.8518		.8269	.029
7H	3	300.1	.8504		.8269	.029
7I	3	300.2	.8541		.8270	.028
2O	2	301.0	.8682		.8285	.025
2H	1	360.0	.8711		.8670	.024
1F	1	360.0	.8806		.8670	.022
10R	3	376.2	.8655		.8687	.026
1H	1	420.0	.8846		.8701	.021
2I	1	420.0	.8709		.8701	.024
1I	1	420.0	.8836		.8701	.022
1G	1	420.0	.8826		.8701	.022
2J	1	31.5 hr	.9047		.8704	.017
10X	3	138.2	.9272		.8704	.012

[a] Reaction temperature = 50.0°C; AIBN Concn. = .5 wt-%; First order rate constant = 1.402 E-03 (l./min): Sawada Equation constants, A = .8704, B = .2020, KKP = 6.513E-02, C = −1.556 E + 01.

Measured cumulative DMWD's corresponding to the main replicates were obtained at 90°C, 0.5 wt-% AIBN, and 45% conversion. It was not possible to measure DMWD's by GPC for the 50°C polymerizations beyond low conversions and into the region of diffusion control. The molecular weights were too large for adequate resolution. Nevertheless, the test of reproducibility was quite severe since at this conversion the polymerization rate is very fast, with the gel effect having been significantly developed. Shrinkage measurements were all made with one or more replicates. Reproducibility data are smumarized in Tables II and III and Figure 2. Conversion data for all of the polymerizations are tabulated in Tables IV to XI. Reproducibility may also be judged by observing these latter tables. These data show that conversion is generally reproducible to better than 1%. However, during the gel effect the reproducibility is much worse. For example, with the polymerization at 50°C, 0.5 wt-% AIBN, and 240 min, the reproducibility is about 5%.

TABLE VII. Gravimetrically Determined and Predicted Conversions[a]

Sample no.	Ampoule type	Time, min	X Exp	X First order	X Sawada	Free volume
11W	2	10.0	.0588	.0603		.192
14A	3	15.0	.0896	.0892		.187
11X	2	20.0	.1157	.1170		.183
14B	3	35.0	.1905	.1955		.171
14D	3	50.0	.2841	.2671	.3217	.156
14E	3	60.1	.3785	.3118	.3784	.139
23C	6	65.0	.4857		.4857	.119
14F	3	70.0	.8317		.6643	.046
14G	3	80.0	.8854		.8848	.033
16F	3	85.0	.8977		.9087	.030
14H	3	90.0	.9030		.9159	.028
14I	3	100.0	.9051		.9187	.028
14C	3	105.0	.9100		.9188	.027
16G	3	114.6	.9123		.9189	.026
16D	3	120.0	.9133		.9189	.026
16B	3	130.0	.9123		.9189	.026
16C	3	140.0	.9218		.9189	.024
16A	3	150.0	.9201		.9189	.024
16I	3	170.0	.9201		.9189	.024
14J	3	217.9	.9221		.9189	.024
16H	3	46.5	.9551		.9189	.015

[a] Reaction temperature = 70.0°C; AIBN Concn. = .3 wt-%; First order rate constant = 6.215 E-03 (l./min); Sawada equation constants: A = .9189, B = .3163, KKP = 4.153 E-01, C = −2.856 E + 01.

TABLE VIII. Gravimetrically Determined and Predicted Conversions[a]

Sample no.	Ampoule type	Time, min	X Exp	X First order	X Sawada	Free volume
19C	3	5.0	.0400	.0365		.195
19A	3	10.0	.0745	.0714		.190
10S	3	20.0	.1407	.1376		.179
19D	3	35.0	.2395	.2282	.3167	.163
15H	3	45.0	.3276	.2832	.3277	.148
15I	3	55.0	.5286		.5237	.111
19B	3	60.1	.7596		.7624	.062
15E	3	63.8	.8692		.8620	.037
18B	6	70.0	.8943		.9110	.031
18G	6	76.4	.9033		.9179	.028
18D	6	80.0	.9115		.9186	.026
18E	6	80.3	.9045		.9186	.028
18C	6	100.0	.9105		.9189	.027
18F	6	186.1	.9311		.9189	.021
18J	6	46.5 hr	.9570		.9189	.015

[a] Reaction temperature = 70.0°C; AIBN Concn. = .5 wt-%; First order rate constant = 7.398 E-03 (l./min); Sawada equation constants: A = .9189, B = .3163, KKP = 5.483 E-01, C = −3.123 E + 01

TABLE IX
Gravimetrically Determined and Predicted Conversions[a]

Sample no.	Ampoule type	Time, min	X Exp	X First order	Free volume
3L	2	81.7	.0251	.0173	.217
3H	2	88.5	.0196	.0187	.218
3J	2	127.8	.0355	.0269	.216
3I	2	127.8	.0350	.0269	.216
3K	2	171.9	.0420	.0360	.215
3E	2	196.9	.0486	.0412	.213
3M	2	203.5	.0497	.0425	.213
3N	2	254.4	.0602	.0529	.212
3B	2	256.4	.0567	.0533	.212
3A	2	302.6	.0681	.0626	.210
3C	2	321.8	.0760	.0664	.209
3D	2	379.6	.0863	.0779	.208
3G	2	895.8	.2576	.1741	.179

[a] Reaction temperature = 90.0°C; AIBN concn. = 0.0 wt-%; first-order rate constant = 2.136 E-04 (l./min).

TABLE X
Gravimetrically Determined and Predicted Conversions[a]

Sample no.	Ampoule type	Time, min	X Exp	X First order	X Sawada	Free volume
23E	6	7.0	.1802	.1833		.192
25H	6	8.0	.2069	.2066		.188
23I	6	8.2	.2117	.2105		.187
25D	6	9.0	.2253	.2292		.184
23B	6	10.1	.2513	.2538		.180
25J	6	11.0	.2715	.2725		.176
23G	6	12.3	.3062	.3004		.170
25I	6	13.0	.3206	.3134		.167
25G	6	15.0	.3675	.3520	.4225	.159
23F	6	16.0	.4036	.3710	.4275	.152
25B	6	17.0	.4274		.4389	.147
25C	6	19.0	.5407		.5234	.125
23H	6	20.0	.6518		.6220	.101
25A	6	21.0	.7284		.7445	.083
25E	6	27.1	.9371		.9589	.031
25F	6	424.0	.9689		.9602	.022

[a] Reaction temperature = 90.0°C; AIBN concn. = .3 wt-%; first order rate constant = 2.893E-02 (l./min); Sawada equation constants: A = .9602, B = .4193, $KKP = 1.705\,\mathrm{E} + 00$, $C = -3.505\,\mathrm{E} + 01$.

The reproducibility of molecular weights involved three different kinds of measurements: molecular weight averages (of interest since they can be measured by other analytical techniques and often correlate with end-use properties of polymers), GPC chromatogram heights (for use in "The Method of Chromatogram Heights" to be discussed later), and the product of normalized GPC heights and gravimetrically determined conversion

TABLE XI
Gravimetrically Determined and Predicted Conversions[a]

Sample no.	Ampoule type	Time, min	X Exp	X First order	X Sawada	Free volume
22C	3	6.0	.1911	.1946		.190
22E	3	7.1	.2265	.2244		.184
22D	3	8.0	.2532	.2505		.180
24F	6	10.0	.3083	.3017		.170
26C	6	10.0	.3040	.3020	.4199	.171
24C	6	12.0	.3746	.3500	.4245	.157
26A	6	13.0	.4077	.3733	.4334	.151
26D	6	14.0	.4603		.4574	.141
26E	6	14.0	.4571		.4574	.142
26G	6	14.0	.4587		.4574	.141
26H	6	14.0	.4569		.4574	.142
26I	6	14.0	.4582		.4574	.141
24A	6	15.0	.5389		.5147	.125
24E	6	16.0	.6331		.6260	.105
24G	6	17.0	.7335		.7609	.082
24B	6	18.	.9007		.8724	.041
26B	6	19.0	.9193		.9235	.036
24D	6	20.1	.9283		.9483	.033
24J	6	27.1	.9407		.9602	.030
24H	6	60.0	.9515		.9602	.027
27A	3	122.0	.9586		.9602	.025
26F	6	400.0	.9663		.9602	.023

[a] Reaction temperature = 90.0°C; AIBN concn. = .5 wt-%; first order rate constant = 3.595 E-02 (l./min); Sawada equation constants: A = .9602, B = .4193, KKP = 1.923E + 00, C = −3.169E + 01.

(for use in "The Method of Differential Chromatograms" to be discussed later). Reproducibilities are shown in Tables II and III and Figure 3. Further information on reproducibility may be found in Tables XII to XVIII.

The central chromatogram heights are highly reproducible whereas the tails have poor reproducibility. This is clearly shown in Figure 3 and in Table III for the corresponding molecular weight averages and was not unexpected. At the onset of diffusion control, the instantaneous DMWD quickly broadens with a resulting production of very high molecular weight polymer. This phenomenon is very difficult to reproduce with any precision because this polymer growth process is associated with a very high rate of polymerization. The time error involved in quenching the reaction is probably sufficient to account for the poor reproducibility. The number-average molecular weight has better reproducibility than the higher molecular weight averages because it depends less on the high molecular weight tail.

Special precautions were taken to ensure that the polymerizations in the ampoules were isothermal. At first, attempts were made to measure temperature directly using thermocouples (types #7 and 8, Fig. 1). These

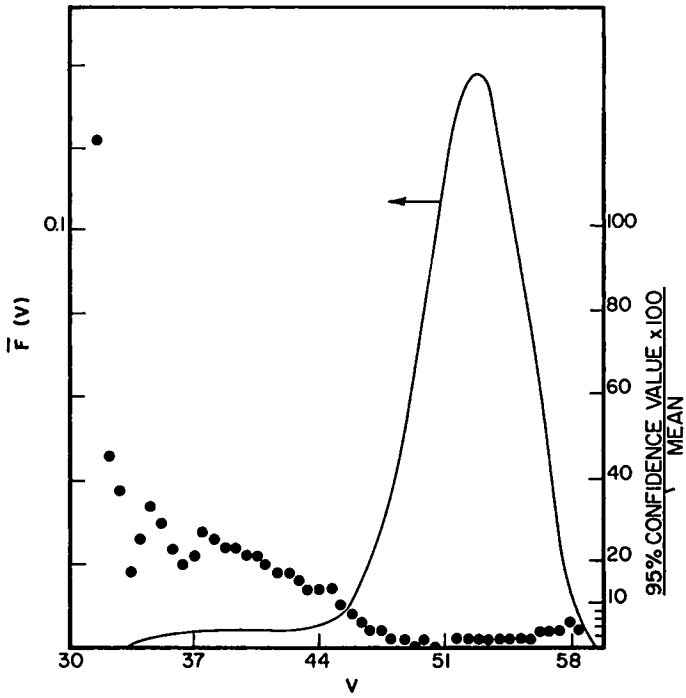

Fig. 3. Mean height values of chromatograms of five-ampoule prepared PMMA samples (nos. 26-D,E,G,H,I; GPC nos. 602-606) and confidence value as a per cent of mean vs. retention volume.

were not successful. Air leaks at the sealed entrance to the ampoule and reaction of the thermocouple with the monomer were some of the problems experienced. However, these rough measurements and theoretical calculations of temperature indicated that there was about a 6°C rise in temperature at the center of a 5-mm-O.D. ampoule (surface-to-volume ratio of 1.63) during the gel effect with a polymerization temperature of 90°C. With a 3-mm-O.D. ampoule, the rise is about 1°C. The most reliable test for isothermal conditions was to compare conversion and molecular weight distribution of polymer produced using ampoules of different surface to volume ratios (refer to Fig. 1 and Tables IV–XVIII).

Although the qualitative variation of conversion with time for the bulk polymerization of MMA is well known, the shape of the cumulative DMWD of PMMA during the gel effect has been the subject of disagreement for more than twenty years. This study has provided considerable evidence that the DMWD is bimodal at high conversions. This agrees with some recent unpublished work of Kawasaki.[13] In our study, DMWD's were measured by GPC throughout the gel effect and showed the growth of a second high molecular weight peak at the onset of diffusion control. This distinctive trend with conversion essentially eliminates other possible causes of bimodal distributions. The presence of high

TABLE XII
Infinite-Resolution Molecular Weight Averages[a]

Sample no.	Time, min	X	GPC no.	Column code	$M_n(\infty)$	$M_w(\infty)$	$M_z(\infty)$	$M_{z+1}(\infty)$	$P(\infty)$
11R	84.6	.0852	628	27	4.52E + 05	1.03E + 06	1.90E + 06	3.15E + 06	2.28
11R	84.6	.0852	640	28	3.89E + 05	1.02E + 06	1.93E + 06	3.31E + 06	2.63
11R	84.6	.0852	686 MP	28	4.37E + 05	1.01E + 06	1.76E + 06	2.68E + 06	2.31
11T	120.0	.1152	649	28	5.48E + 05	1.22E + 06	2.06E + 06	2.97E + 06	2.23
11P	200.0	.2023	642	28	4.92E + 05	1.26E + 06	2.42E + 06	3.97E + 06	2.56
11C	250.0	.3273	641	28	5.96E + 05	2.03E + 06	4.12E + 06	6.04E + 06	3.40

[a] T = 50°C; AIBN = 0.3 wt-%.

TABLE XIII
Infinite-Resolution Molecular Weight Averages[a]

Sample no.	Time, min	X	GPC no.	Column code	$M_n(\infty)$	$M_w(\infty)$	$M_z(\infty)$	$M_{z+1}(\infty)$	$P(\infty)$
4I	84.6	.1036	560 MP	25	3.67E + 05	1.22E + 06	3.75E + 06	9.78E + 06	3.32
4I	84.6	.1036	569 MP	25	3.84E + 05	1.25E + 06	4.15E + 06	1.24E + 07	3.25
4I	84.6	.1036	626	27	3.91E + 05	9.85E + 05	2.17E + 06	4.44E + 06	2.52
4I	84.6	.1036	648	28	3.68E + 05	9.22E + 05	1.74E + 06	2.79E + 06	2.50
4H	124.2	.1449	559 MP	25	3.54E + 05	1.02E + 06	2.26E + 06	4.37E + 06	2.88
4H	124.2	.1449	650	28	3.76E + 05	9.58E + 05	1.96E + 06	3.69E + 06	2.55
12D	150.0	.1671	700	28	3.69E + 05	9.34E + 05	1.75E + 06	2.84E + 06	2.52
4G	187.5	.2433	643	28	4.12E + 05	1.32E + 06	2.96E + 06	5.03E + 06	3.20

[a] T = 50°C; AIBN = 0.391 wt-%.

TABLE XIV
Infinite-Resolution Molecular Weight Averages[a]

Sample no.	Time, min	X	GPC no.	Column code	M_n (∞)	M_w (∞)	M_z (∞)	M_{z+1} (∞)	P (∞)
10A	60.0	.0801	627	27	3.38E + 05	7.19E + 05	1.21E + 06	1.77E + 06	2.12
10A	60.0	.0801	647	28	2.96E + 05	7.20E + 05	1.24E + 06	1.81E + 06	2.43
10A	60.0	.0801	685 MP	28	2.76E + 05	7.39E + 05	1.36E + 06	2.18E + 06	2.67
10K	84.6	.1117	644	28	3.24E + 05	8.04E + 05	1.48E + 06	2.39E + 06	2.48
9F	120.0	.1481	646	28	3.68E + 05	8.41E + 05	1.53E + 06	2.50E + 06	2.28
10I	210.0	.3492	645	28	4.96E + 05	1.81E + 06	4.63E + 06	9.85E + 06	3.65

[a] T = 50°C; AIBN = 0.5 wt-%.

TABLE XV
Infinite-Resolution Molecular Weight Averages[a]

Sample no.	Time, min	X	GPC no.	Column code	M_n (∞)	M_w (∞)	M_z (∞)	M_{z+1} (∞)	P (∞)
11W	10.0	.0588	583	27	1.40E + 05	3.09E + 05	5.28E + 05	7.79E + 05	2.20
11W	10.0	.0588	612	27	1.43E + 05	3.14E + 05	5.41E + 05	8.05E + 05	2.19
11W	10.0	.0588	634	28	1.52E + 05	3.31E + 05	5.90E + 05	9.19E + 05	2.18
14A	15.0	.0896	593	27	1.44E + 05	3.06E + 05	5.18E + 05	7.57E + 05	2.13
14A	15.0	.0896	613	27	1.41E + 05	3.17E + 05	5.87E + 05	9.96E + 05	2.25
14A	15.0	.0896	670 MP	28	1.44E + 05	3.19E + 05	5.77E + 05	9.42E + 05	2.22
11X	20.0	.1157	584	27	1.39E + 05	2.98E + 05	4.98E + 05	7.15E + 05	2.14
14E	60.1	.3785	588	27	1.66E + 05	6.75E + 05	3.10E + 06	6.69E + 06	4.07
14E	60.1	.3785	637	28	1.61E + 05	7.39E + 05	3.45E + 06	7.38E + 06	4.58
14E	60.1	.3785	669 MP	28	1.58E + 05	6.61E + 05	2.79E + 06	6.21E + 06	4.18
23C	65.0	.4857	589	27	2.05E + 05	1.02E + 06	3.73E + 06	6.54E + 06	5.00
14F	70.0	.8317	595	27	3.02E + 05	1.61E + 06	3.88E + 06	5.81E + 06	5.31
14H	90.0	.9030	586	27	3.52E + 05	1.81E + 06	4.06E + 06	5.84E + 06	5.12
16H	46.5 hrs.	.9551	598	27	3.73E + 05	1.82E + 06	4.09E + 06	5.92E + 06	4.88

[a] T = 70°C; AIBN = 0.3 wt-%.

TABLE XVI
Infinite-Resolution Molecular Weight Averages[a]

Sample no.	Time, min	X	GPC no.	Column code	$M_n(\infty)$	$M_w(\infty)$	$M_z(\infty)$	$M_{z+1}(\infty)$	$P(\infty)$
19C	5.0	.0400	600	27	1.23E + 05	2.57E + 05	4.34E + 05	6.29E + 05	2.09
19C	5.0	.0400	622	27	1.11E + 05	2.79E + 05	6.29E + 05	1.50E + 06	2.51
19A	10.0	.0745	599	27	1.14E + 05	2.45E + 05	4.23E + 05	6.44E + 05	2.14
19A	10.0	.0745	620	27	1.05E + 05	2.74E + 05	7.09E + 05	1.98E + 06	2.60
19A	10.0	.0745	671 MP	28	1.09E + 05	2.34E + 05	3.82E + 05	5.28E + 05	2.14
10S	20.0	.1407	585	27	1.11E + 05	2.88E + 05	9.70E + 05	3.01E + 06	2.59
10S	20.0	.1407	611	27	1.17E + 05	2.84E + 05	9.86E + 05	3.33E + 06	2.44
10S	20.0	.1407	636	28	1.12E + 05	2.39E + 05	4.04E + 05	5.83E + 05	2.14
15H	45.0	.3276	587	27	1.24E + 05	4.01E + 05	2.47E + 06	6.88E + 06	3.24
15H	45.0	.3276	635	28	1.21E + 05	3.81E + 05	1.94E + 06	5.45E + 06	3.16
15I	55.0	.5286	576	27	1.85E + 05	9.44E + 05	3.85E + 06	6.92E + 06	5.10
15I	55.0	.5286	581	27	1.68E + 05	8.52E + 05	3.31E + 06	5.83E + 06	5.06
19B	60.1	.7596	573	27	2.23E + 05	1.18E + 06	3.14E + 06	4.92E + 06	5.30
19B	60.1	.7596	582	27	2.26E + 05	1.17E + 06	3.19E + 06	5.14E + 06	5.15
18B	70.0	.8943	673 MP[b]	28	2.81E + 05	1.52E + 06	3.69E + 06	5.70E + 06	5.40
18B	70.0	.8943	678 MP[b]	28	2.71E + 05	1.47E + 06	3.51E + 06	5.28E + 06	5.42
18B	70.0	.8943	672 MP[c]	28	2.64E + 05	1.44E + 06	3.39E + 06	5.07E + 06	5.45
18B	70.0	.8943	677 MP[c]	28	2.59E + 05	1.37E + 06	3.20E + 06	4.73E + 06	5.29
18E	80.3	.9045	570	27	2.82E + 05	1.40E + 06	3.36E + 06	5.11E + 06	4.98

18J	46.5 hr	.9570	610	27	2.76E + 05	1.40E + 06	3.52E + 06	5.60E + 06	5.09
18J	46.5 hr	.9570	615	27	2.55E + 05	1.38E + 06	3.44E + 06	5.37E + 06	5.41
18J	46.5 hr	.9570	616	27	2.57E + 05	1.39E + 06	3.48E + 06	5.49E + 06	5.40
18J	46.5 hr	.9570	617	27	2.60E + 05	1.36E + 06	3.37E + 06	5.20E + 06	5.25
18J	46.5 hr	.9570	618	27	2.50E + 05	1.35E + 06	3.33E + 06	5.11E + 06	5.42
18J	46.5 hr	.9570	619	27	2.63E + 05	1.39E + 06	3.47E + 06	5.43E + 06	5.29
18J	46.5 hr	.9570	631	28	2.57E + 05	1.44E + 06	3.45E + 06	5.20E + 06	5.61
18J	46.5 hr	.9570	717[d]	28	2.76E + 05	1.42E + 06	3.40E + 06	5.15E + 06	5.16
18J	46.5 hr	.9570	668 MP	28	2.72E + 05	1.46E + 06	3.53E + 06	5.32E + 06	5.37

[a] $T = 70°C$; AIBN = 0.5 wt-%.
[b] 3-mm-O.D. ampoule section.
[c] 2-mm-O.D. ampoule section.
[d] Heated previous to injection.

TABLE XVII
Infinite-Resolution Molecular Weight Averages[a]

Sample no.	Time, min	X	GPC no.	Column code	$M_n(\infty)$	$M_w(\infty)$	$M_z(\infty)$	$M_{z+1}(\infty)$	$P(\infty)$
23E	7.0	.1802	579	27	6.03E + 04	1.14E + 05	1.82E + 05	2.55E + 05	1.90
23E	7.0	.1802	638	28	6.05E + 04	1.17E + 05	1.90E + 05	2.72E + 05	1.94
23E	7 0	.1802	681 MP	28	4.96E + 04	1.11E + 05	1.83E + 05	2.61E + 05	2.24
23I	8.2	.2117	601	27	6.06E + 04	1.17E + 05	1.89E + 05	2.69E + 05	1.92
23I	8.2	.2117	639	28	6.07E + 04	1.19E + 05	1.99E + 05	3.01E + 05	1.97
23I	8.2	.2117	682 MP	28	4.92E + 04	1.14E + 05	1.92E + 05	2.79E + 05	2.31
23B	10.1	.2513	590	27	6.28E + 04	1.20E + 05	1.99E + 05	3.01E + 05	1.92
23F	16.0	.4036	575	27	6.54E + 04	1.30E + 05	2.08E + 05	2.85E + 05	1.99
25C	19.0	.5407	713	28	7.86E + 04	3.46E + 05	2.17E + 06	5.14E + 06	4.40
23H	20.0	.6518	580	27	9.94E + 04	5.41E + 05	2.67E + 06	5.76E + 06	5.44
23H	20.0	.6518	712	28	9.45E + 04	4.67E + 05	1.97E + 06	3.83E + 06	4.94
25A	21.0	.7284	578	27	1.02E + 05	4.02E + 05	1.19E + 06	2.21E + 06	3.94
25E	27.0	.9371	608	27	1.31E + 05	5.65E + 05	1.48E + 06	2.69E + 06	4.33
25F	424.0	.9689	607	27	1.27E + 05	5.45E + 05	1.35E + 06	2.25E + 06	4.28
25F	424.0	.9689	714	28	1.18E + 05	5.64E + 06	1.45E + 06	2.44E + 06	4.77

[a] T = 90°C; AIBN = 0.3 wt-%.

TABLE XVIII
Infinite-Resolution Molecular Weight Averages[a]

Sample no.	Time, min	X	GPC no.	Column code	$M_n(\infty)$	$M_w(\infty)$	$M_z(\infty)$	$M_{z+1}(\infty)$	$P(\infty)$
22C	6.0	.1911	592	27	4.87E + 04	9.35E + 04	1.52E + 05	2.21E + 05	1.92
22C	6.0	.1911	632	28	4.87E + 04	9.49E + 04	1.62E + 05	2.58E + 05	1.95
22C	6.0	.1911	666 MP	28	3.28E + 04	8.70E + 04	1.52E + 05	2.37E + 05	2.65
22E	7.1	.2265	574	27	5.13E + 04	9.15E + 04	1.44E + 05	2.03E + 05	1.78
22E	7.1	.2265	667 MP	28	3.42E + 04	8.60E + 04	1.47E + 05	2.20E + 05	2.52
22D	8.0	.2532	596	27	4.91E + 04	9.18E + 04	1.48E + 05	2.18E + 05	1.87
22D	8.0	.2532	597	27	4.85E + 04	9.17E + 04	1.48E + 05	2.13E + 05	1.89
22D	8.0	.2532	630	28	4.85E + 04	9.28E + 04	1.51E + 05	2.19E + 05	1.91
22D	8.0	.2532	683 MP	28	3.93E + 04	8.69E + 04	1.45E + 05	2.09E + 05	2.20
26C	10.0	.3040	716	28	4.79E + 04	9.35E + 04	1.53E + 05	2.20E + 05	1.95
26D	14.0	.4603	602	27	5.96E + 04	2.01E + 05	1.24E + 06	3.08E + 06	3.37
26D	14.0	.4603	633	28	5.37E + 04	1.92E + 05	1.28E + 06	3 30E + 06	3.58
26D	14.0	.4603	680 MP	28	4.05E + 04	2.25E + 05	2.67E + 06	7.99E + 06	5.54
26E	14.0	.4571	603	27	5.72E + 04	2.02E + 05	1.49E + 06	3.98E + 06	3.52
26E	14.0	.4571	655 MP[b]	27	4.66E + 04	1.84E + 05	1.31E + 06	3.72E + 06	3.94
26E	14.0	.4571	656 MP[c]	27	4.74E + 04	2.18E + 05	1.78E + 06	4.22E + 06	4.61
26G	14.0	.4587	604	27	5.73E + 04	2.01E + 05	1.78E + 06	5.20E + 06	3.51
26H	14.0	.4569	605	27	5.52E + 04	1.47E + 05	1.03E + 06	4.65E + 06	2.66
26I	14.0	.4582	606	27	6.16E + 04	2.28E + 05	1.68E + 06	4.15E + 06	3.70
26I	14.0	.4582	614	27	5.80E + 04	1.94E + 05	1.38E + 06	3.61E + 06	3.35
24A	15.0	.5389	594	27	6.25E + 04	2.47E + 05	1.39E + 06	3.13E + 06	3.95
24E	16.0	.6331	572	27	7.27E + 04	3.43E + 05	1.64E + 06	3.40E + 06	4.72
24G	17.0	.7335	591	27	8.09E + 04	2.97E + 05	8.51E + 05	1.52E + 06	3.67
24D	20.1	.9283	571	27	9.47E + 04	3.89E + 05	1.00E + 06	1.77E + 06	4.10
24D	20.1	.9283	651 MP[b]	27	7.71E + 04	3.73E + 05	9.97E + 05	1.87E + 06	4.84
24D	20.1	.9283	665 MP[b]	27	7.96E + 04	3.76E + 05	9.54E + 05	1.58E + 06	4.72
24D	20.1	.9283	652 MP[c]	27	7.78E + 04	3.74E + 05	9.29E + 05	1.50E + 06	4.81
26F	400.0	.9663	609	27	1.04E + 05	3.98E + 05	9.70E + 05	1.61E + 06	3.84

[a] $T = 90°C$; AIBN = 0.5 wt-%.
[b] 3-mm-O.D. ampoule section.
[c] 2-mm-O.D. ampoule section.

molecular weight PMMA in the monomer produced during storage at low temperatures would give a bimodal DMWD even at low conversions. Axial dispersion or some other GPC phenomenon (such as negative adsorption mentioned previously[7]) can be eliminated as a cause because of our methods of GPC calibration and interpretation. Mathematical artifacts resulting from resolution correction methods which have misled previous investigators[8] have been investigated and avoided with the development of new methods of using GPC data.

Molecular aggregation can affect GPC chromatograms. This was demonstrated with PVC.[9] To test for similar aggregation in PMMA, a bimodal sample was heated in THF at 90°C for 10 min. The PMMA in THF was cooled to room temperature and reinjected in the GPC. The resulting GPC chromatogram was unchanged. Some PMMA samples were analyzed by NMR and found to have expected tacticity (see Table XXVIII). It appears that the PMMA produced in this investigation did not form molecular aggregates.

We were unable to detect branching in the PMMA produced at high conversions. At very high conversions, the instantaneous molecular weight averages decreased with conversion. This was a result of monomer depletion. Had branching been important, the molecular weight averages would have continued to increase with conversion.[10] We cannot be sure that short-chain branching and some long-chain branching did not occur.

RESULTS AND DISCUSSION

Model Application to the Onset of the Gel Effect

Conversion

The rate of polymerization showed a first-order dependence on monomer concentration to quite high conversions. The conversions are tabulated in Tables IV to XI. The pseudo first-order rate constants were obtained using a least-squares fit of ln $(1 - X)$ versus time to obtain K_1 according to eq. (9). Our K_1 values are in good agreement with literature values (refer to Fig. 4). A least-squares fit of this line gives

$$\ln K_1 = 30.13 - \frac{9.63 \times 10^3}{T}$$

with an overall activation energy of 19.13 kcal/mole, with T in °K. This demonstrates that rate is first order with respect to monomer and is proportional to the square root of the initiator concentration. Over these ranges of polymerization time, the consumption of AIBN can be neglected.

The quantity free volume was examined in an attempt to find a criterion for diffusion control. Free volume is a measure of voids or holes in the liquid that permit movement of molecules. At the glass transition temperature, the free volume is 0.025. Molecular weight of a polymer plays an insignificant part in the calculation of free volume at each conversion if the molecular weights are not too low while the conversion is not too high.[1]

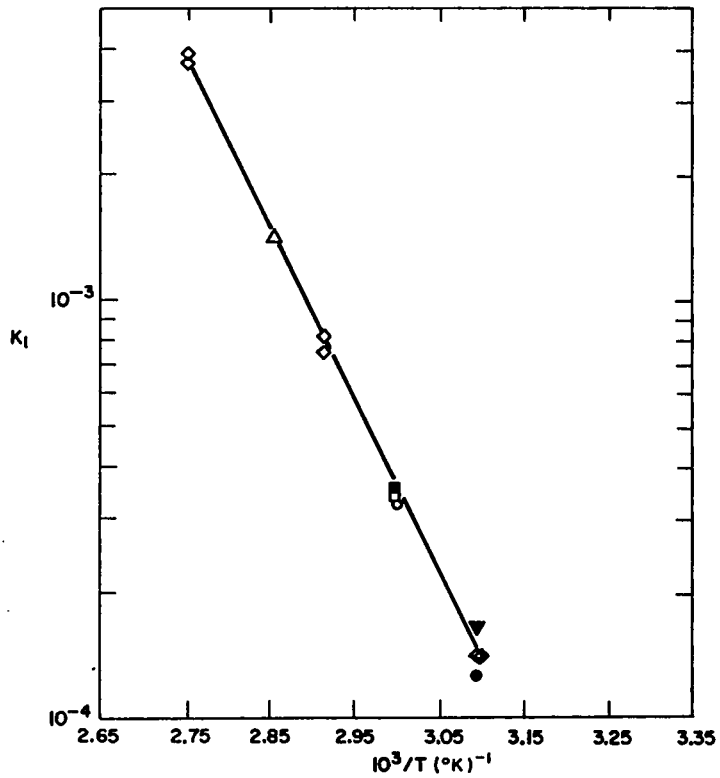

Fig. 4. $K_1(=\sqrt{2fk_d/k_tk_p})$ vs. $10^3/T$. Symbols and reference sources: (◇) this study; (□) 16; (○) 18; (△) 99, ref. 14; (■) 17; (●) 15; (▼) 105, ref. 14.

Our polymerizations lie within these limits. Free volume was therefore calculated from conversion and reaction temperature assuming $T_{gp} = T_{g\infty}$ (that is, free volume does not depend on molecular weight). From an examination of Tables IV to XI, it is evident that the onset of gel effect occurs consistently at a free volume of about 0.151. We define the onset of gel effect to be the conversion where rate of polymerization deviates from a first-order monomer dependence. This is the conversion given by the Sawada constant b.[11]

Molecular Weight Distribution

The kinetic model was fitted to our GPC data using a new method of data interpretation. This was the "Method of Chromatogram Heights."

Using the Method of Chromatogram Heights and, in turn, a three-, two-, and single-variable search on all of the low-conversion GPC chromatograms, it was established that disproportionation was the dominant mode of termination and that transfer reactions had virtually no effect on the molecular weights. Results of the single-variable search are tabulated in Tables XIX to XXV. Molecular weight averages are generally

TABLE XIX
α_1 by the Method ofChromatogram Heights[a]

Sample no.	Time, min	X	GPC no.	Column code	$M_n(\infty)$	$M_{n\ \text{model}}$	$M_w(\infty)$	$M_{w\ \text{model}}$	α_1
11R	84.6	.0852	628	27	4.52E + 05	5.04E + 05	1.03E + 06	1.01E + 06	1.837E − 04
11R	84.6	.0852	640	28	3.89E + 05	5.13E + 05	1.02E + 06	1.03E + 06	1.805E − 04
11R	84.6	.0852	686 MP	28	4.37E + 05	5.30E + 05	1.01E + 06	1.06E + 06	1.747E − 04
11T	120.0	.1152	649	28	5.48E + 05	5.90E + 05	1.22E + 06	1.19E + 06	1.522E − 04
11P	200.0	.2023	642	28	4.92E + 05	6.12E + 05	1.26E + 06	1.24E + 06	1.341E − 04

[a] $T = 50°C$; AIBN = 0.3 wt-%.

TABLE XX
α_1 by the Method of Chromatogram Heights[a]

Sample no.	Time, min	X	GPC no.	Column code	$M_n(\infty)$	$M_{n\ \text{model}}$	$M_w(\infty)$	$M_{w\ \text{model}}$	α_1
4I	84.6	.1036	560 MP	25	3.67E + 05	5.03E + 05	1.22E + 06	1.01E + 06	1.806E − 04
4I	84.6	.1036	569 MP	25	3.84E + 05	5.15E + 05	1.25E + 06	1.03E + 06	1.764E − 04
4I	84.6	.1036	626	27	3.91E + 05	4.32E + 05	9.85E + 05	8.67E + 05	2.103E − 04
4I	84.6	.1036	648	28	3.68E + 05	4.47E + 05	9.22E + 05	8.98E + 05	2.032E − 04
4H	124.2	.1449	559 MP	25	3.54E + 05	4.80E + 05	1.02E + 06	9.66E + 05	1.816E − 04
4H	124.2	.1449	650	28	3.76E + 05	4.48E + 05	9.58E + 05	9.02E + 05	1.946E − 04
12D	150.0	.1671	700	28	3.69E + 05	4.51E + 05	9.34E + 05	9.10E + 05	1.888E − 04
4G	187.5	.2433	643	28	4.12E + 05	5.53E + 05	1.32E + 06	1.13E + 06	1.416E − 04

[a] $T = 50°C$; AIBN = 0.391 wt-%.

TABLE XXI
α_1 by the Method of Chromatogram Heights[a]

Sample no.	Time, min	X	GPC no.	Column code	$M_n(\infty)$	$M_{n\ \text{model}}$	$M_w(\infty)$	$M_{w\ \text{model}}$	α_1
10A	60.0	.0801	627	27	3.38E + 05	3.40E + 05	7.19E + 05	6.81E + 05	2.735E − 04
10A	60.0	.0801	647	28	2.96E + 05	3.65E + 05	7.20E + 05	7.32E + 05	2.547E − 04
10A	60.0	.0801	685 MP	28	2.76E + 05	3.62E + 05	7.39E + 05	7.26E + 05	2.566E − 04
10K	84.6	.1117	644	28	3.24E + 05	3.81E + 05	8.04E + 05	7.65E + 05	2.365E − 04
9F	120.0	.1481	646	28	3.68E + 05	4.08E + 05	8.40E + 05	8.22E + 05	2.129E − 04

[a] $T = 50°C$; AIBN = 0.5 wt-%.

TABLE XXII
α_1 by the Method of Chromatogram Heights[a]

Sample no.	Time, min	X	GPC no.	Column code	$M_n(\infty)$	$M_{n\ \text{model}}$	$M_w(\infty)$	$M_{w\ \text{model}}$	α_1
11W	10.0	.0588	583	27	1.40E + 05	1.45E + 05	3.09E + 05	2.90E + 05	6.549E − 04
11W	10.0	.0588	612	27	1.43E + 05	1.47E + 05	3.14E + 05	2.94E + 05	6.463E − 04
11W	10.0	.0588	634	28	1.52E + 05	1.48E + 05	3.32E + 05	2.96E + 05	6.429E − 04
14A	15.0	.0896	593	27	1.44E + 05	1.40E + 05	3.06E + 05	2.81E + 05	6.587E − 04
14A	15.0	.0896	613	27	1.41E + 05	1.43E + 05	3.17E + 05	2.87E + 05	6.444E − 04
14A	15.0	.0896	670 MP	28	1.44E + 05	1.43E + 05	3.19E + 05	2.87E + 05	6.436E − 04
11X	20.0	.1157	584	27	1.39E + 05	1.43E + 05	2.98E + 05	2.86E + 05	6.305E − 04

[a] $T = 70°C$; AIBN = 0.3 wt-%.

TABLE XXIII
α_1 by the Method of Chromatogram Heights[a]

Sample no.	Time, min	X	GPC no.	Column code	$M_n(\infty)$	$M_{n\ \text{model}}$	$M_w(\infty)$	$M_{w\ \text{model}}$	α_1
19C	5.0	.0400	600	27	1.23E + 05	1.27E + 05	2.57E + 05	2.54E + 05	7.612E − 04
19C	5.0	.0400	622	27	1.11E + 05	1.25E + 05	2.79E + 05	2.50E + 05	7.739E − 04
19A	10.0	.0745	599	27	1.14E + 05	1.14E + 05	2.45E + 05	2.29E + 05	8.198E − 04
19A	10.0	.0745	620	27	1.05E + 05	1.18E + 05	2.73E + 05	2.36E + 05	7.930E − 04
19A	10.0	.0745	671 MP	28	1.09E + 05	1.14E + 05	2.34E + 05	2.28E + 05	8.227E − 04

[a] T = 70°C; AIBN = 0.5 wt-%.

TABLE XXIV
α_1 by the Method of Chromatogram Heights[a]

Sample no.	Time, min	X	GPC no.	Column code	$M_n(\infty)$	$M_{n\ \text{model}}$	$M_w(\infty)$	$M_{w\ \text{model}}$	α_1
23E	7.0	.1802	579	27	6.03E + 04	5.38E + 04	1.14E + 05	1.08E + 05	1.570E − 03
23E	7.0	.1802	638	28	6.05E + 04	5.56E + 04	1.17E + 05	1.12E + 05	1.519E − 03
23E	7.0	.1802	681 MP	28	4.96E + 04	5.37E + 04	1.11E + 05	1.08E + 05	1.572E − 03
23I	8.17	.2117	601	27	6.06E + 04	5.52E + 04	1.17E + 05	1.12E + 05	1.480E − 03
23I	8.17	.2117	639	28	6.07E + 04	5.65E + 04	1.19E + 05	1.15E + 05	1.444E − 03
23I	8.17	.2117	682 MP	28	4.92E + 04	5.54E + 04	1.14E + 05	1.12E + 05	1.473E − 03
23B	10.12	.2513	590	27	6.28E + 04	5.60E + 04	1.20E + 05	1.14E + 05	1.394E − 03

[a] T = 90°C; AIBN = 0.3 wt-%.

TABLE XXV
α_1 by the Method of Chromatogram Heights[a]

Sample no.	Time, min	X	GPC no.	Column code	$M_n(\infty)$	$M_{n\ \text{model}}$	$M_w(\infty)$	$M_{w\ \text{model}}$	α_1
22C	6.02	.1911	592	27	4.87E + 04	4.37E + 04	9.35E + 04	8.85E + 04	1.908E − 03
22C	6.02	.1911	632	28	4.87E + 04	4.43E + 04	9.49E + 04	8.97E + 04	1.882E − 03
22C	6.02	.1911	666 MP	28	3.28E + 04	4.25E + 04	8.70E + 04	8.60E + 04	1.963E − 03
22E	7.07	.2265	574	27	5.13E + 04	4.29E + 04	9.15E + 04	8.72E + 04	1.872E − 03
22E	7.07	.2265	667 MP	28	3.42E + 04	4.10E + 04	8.60E + 04	8.34E + 04	1.958E − 03
22D	8.02	.2532	596	27	4.91E + 04	4.32E + 04	9.17E + 04	8.83E + 04	1.803E − 03
22D	8.02	.2532	597	27	4.86E + 04	4.34E + 04	9.17E + 04	8.87E + 04	1.794E − 03
22D	8.02	.2532	630	28	4.85E + 04	4.41E + 04	9.28E + 04	9.00E + 04	1.769E − 03
22D	8.02	.2532	683 MP	28	3.93E + 04	4.08E + 04	8.69E + 04	8.33E + 04	1.912E − 03
26C	10.00	.3040	697	28	4.79E + 04	4.48E + 04	9.35E + 04	9.26E + 04	1.638E − 03

[a] T = 90°C; AIBN = 0.5 wt-%.

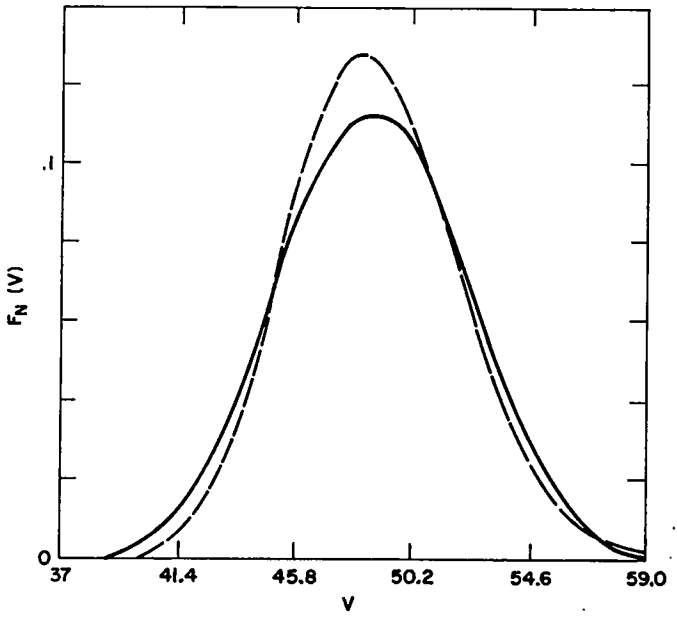

Fig. 5. Result of a single-variable search for α_1 using the method of chromatogram heights: (——) chromatogram of sample no. 11X (GPC no. 584); (– – –) chromatogram from α_1 search.

in good agreement with those predicted by the model. Model chromatograms are always higher and narrower than those measured by GPC. (A typical results is shown in Fig. 5.) This can be explained as a result of axial dispersion in GPC, which tends to broaden chromatograms. With the seven and nine GPC columns in series used here, corrections to molecular weight averages are of the order of 10% for M_n and -5% for M_w.

The quantity

$$A' = \frac{1}{2}(1 + \lambda)\frac{k_t}{k_p^2} = \frac{\alpha_1 M_0 \cdot 60}{\frac{dX}{dt}}$$

where λ is unity when disproportionation is the dominant mode of termination and λ is zero when combination dominantes, was extracted from α_1 obtained in the single-variable search and compared with literature values in Figure 6. Our values at 70°C and 90°C are somewhat higher than the few literature values. However, they provide a better straight line with literature values at lower temperatures. A least-squares fit of this line gives

$$\ln A' = -4.609 + 2.960\left(\frac{10^3}{T}\right)$$

giving an overall activation energy of -5.88 kcal/mole.

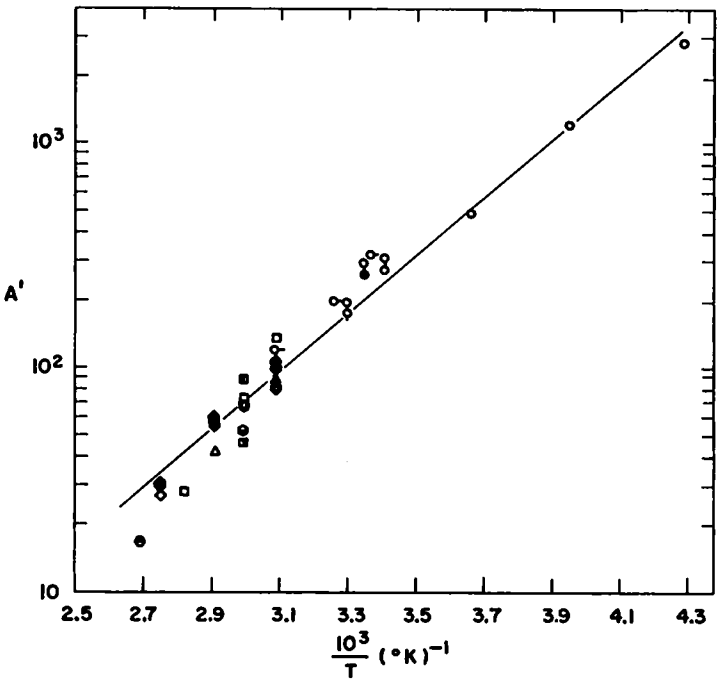

Fig. 6. $A' = (.5(1.+ \lambda)k_{td}/k_p^2)$ vs. $10^3/T$: (◇) this study; (○) 18; (□) 21; (⊙) 22; (△) 99 in ref. 14; (◒) 19; (◧) 16; (○) 23; (▲) 15; (◓) 104 in ref. 14; (◨) 17; (⊙) 24; (▲) 94 in ref. 14; (▽) 20; (◒). 25.

Typical measured and predicted $\bar{M}_n$ and $\bar{M}_w$ values are shown in Figure 7. At low conversions, agreement is good. At higher conversions, the rapid increase in M_w is a consequence of diffusion control.

Model Application During the Gel Effect

Conversion

The Sawada equation[11] was applied as follows. The limiting conversion a was calculated using eqs. (16) and (17). The conversion at the onset of the gel effect b was calculated using eq. (10) with $V_f = 0.151$. To evaluate the constants K and C, a least-squares fit of $\ln \left\{\frac{X - b}{a - X}\right\}$ versus t during the gel effect was made. Then

$$K = \frac{2.303B_2}{(a - b)} \quad \text{and} \quad C = \frac{2.303B_1}{(a - b)}$$

where

$$\ln \left\{\frac{X - b}{a - X}\right\} = B_1 + B_2 t.$$

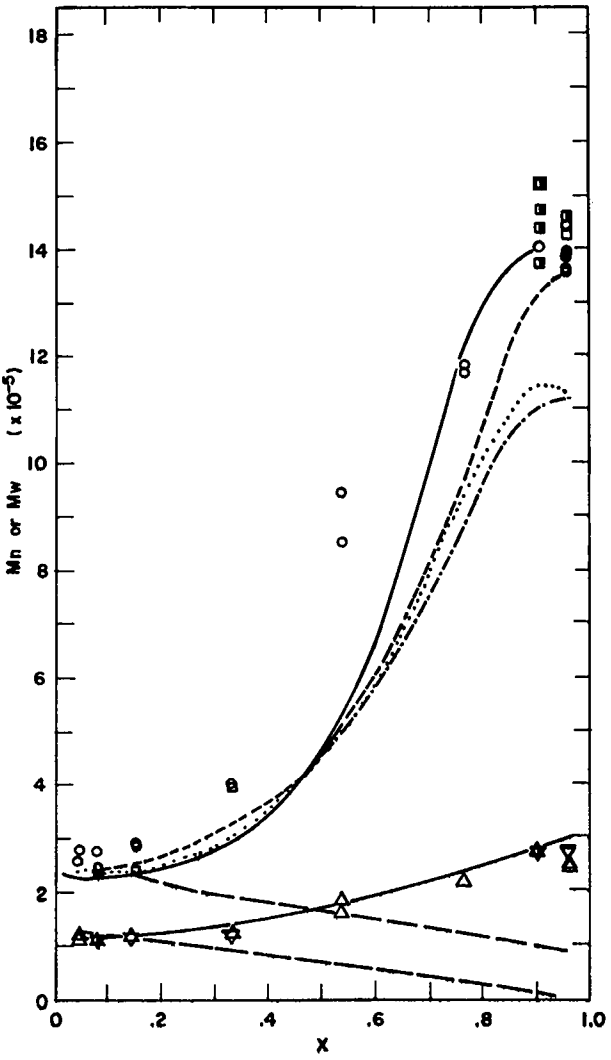

Fig. 7. Experimental and model M_n and M_w at 70°C, 0.5 wt. % AIBN: (○) $M_w(\infty)$, code 27;* (△) $M_n(\infty)$, code 27;* (□) $M_w(\infty)$, code 28;* (▽) $M_n(\infty)$, code 28;* (◑) $M_w(\infty)$, code 27;** (▲) $M_n(\infty)$, code 27;** (■) $M_w(\infty)$, code 28;** (▼) $M_n(\infty)$, code 28;** α_1 from (- — - —) fit #1 and (. . .) fit # 2 method of differential chromatograms; (- - -) 2 variable search and (——) 3 variable search method of chromatogram heights; (— — —) conventional kinetics (constant k_{td}). α_1 from: (——) {fit #1, #2, 2 variable search and 3 variable search}.

* Precipitated polymer. ** Monomer-polymer mixture.

An inspection of Tables IV to XI shows that a free volume of 0.025 is reached near limiting conversion. The glass transition point appears to give a useful criterion for the estimation of the limiting conversion. Apparently long polymerization times permit Van der Waals contraction with the free volume decreasing to values less than 0.025.

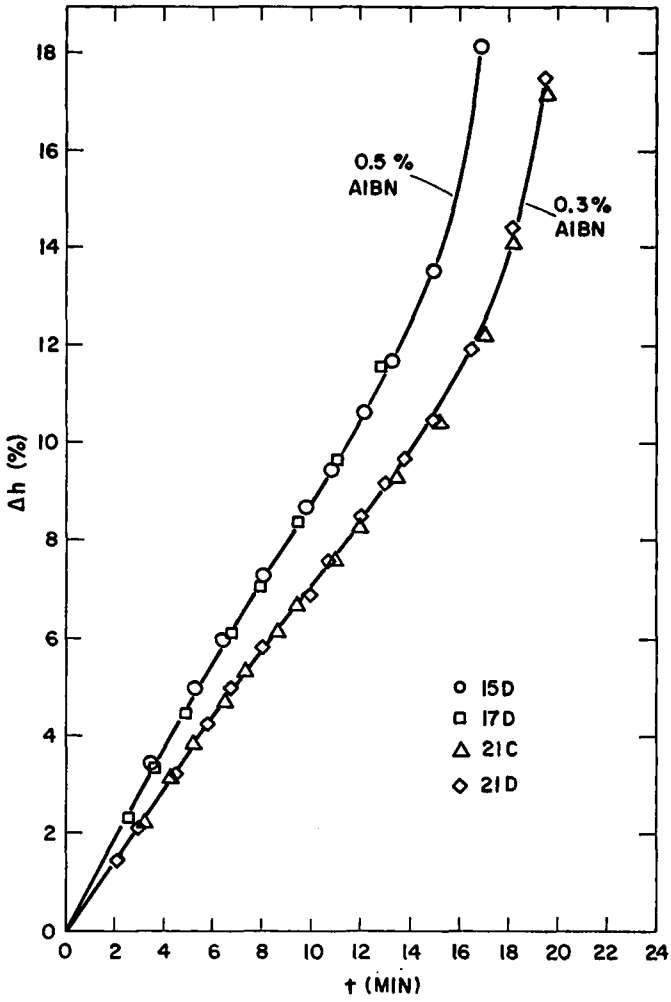

Fig. 8. Per cent contraction vs. time, 90°C, 0.3% and 0.5 wt-% AIBN.

The contraction parameter ϵ was determined from data on per cent shrinkage versus conversion. Figures 8 and 9 illustrate typical plots; ϵ values determined here and from the literature are tabulated in Table XXVI. Our ϵ values are generally higher. Two possible reasons for

TABLE XXVI
Shrinkage in MMA Polymerization (Present Study)

Temp., °C	ϵ (this study)	$\epsilon = \frac{\rho_{monomer}}{\rho_{polymer}} - 1$[a]
50	−.244	−.228
70	−.265	−.246
90	−.295	−.264

[a] For details refer to reference 1.

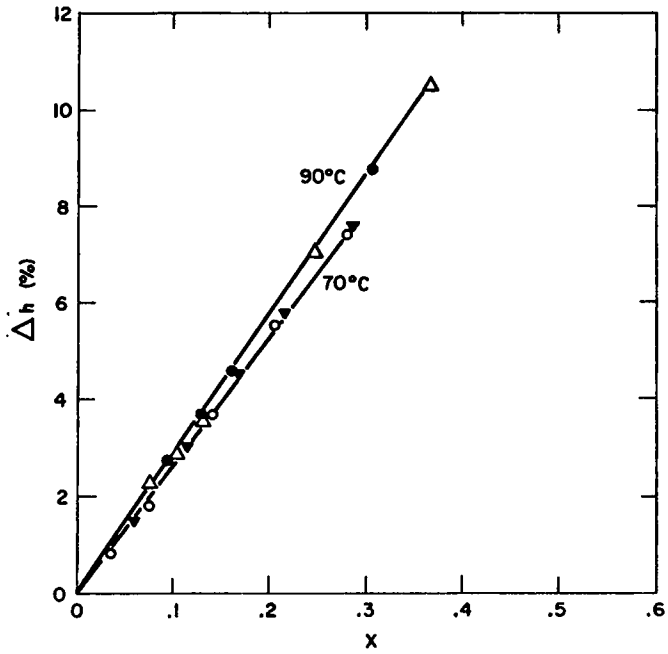

Fig. 9. Per cent contraction vs. conversion, 70°C and 90°C: (▼△) .3% AIBN; (O●) .5 wt-% AIBN.

the discrepancy are that literature values are calculated assuming complete conversion of monomer, an invalid assumption; and secondly shrinkage in our experiments occurred in vacuum. The effect of the differences in the ϵ values on predicted DMWD and molecular weight averages is small.

Molecular Weight Distribution

At low conversions, the method of differential chromatograms and the method of chromatogram heights are effectively the same. However, at higher conversions, the method of differential chromatograms proved invaluable. In applying this method, it was assumed that termination by disproportionation was the dominant mode of termination and that transfer reactions had negligible effect on the DMWD at high conversions. The cumulative chromatograms from which the differential chromatograms were obtained are shown in Figures 10 to 13.

Initial attempts to guess the functional dependence of α_1 on conversion and apply the method of chromatogram heights gave only limited success. The method of differential chromatograms does not require such a function. A single variable search for α_1 was made to match each instantaneous GPC chromatogram. A typical result is shown in Figure 14. The α_1 values obtained at 70°C and 0.5% AIBN are shown in Figure 15. The ends of the horizontal bars give the conversions at which cumulative

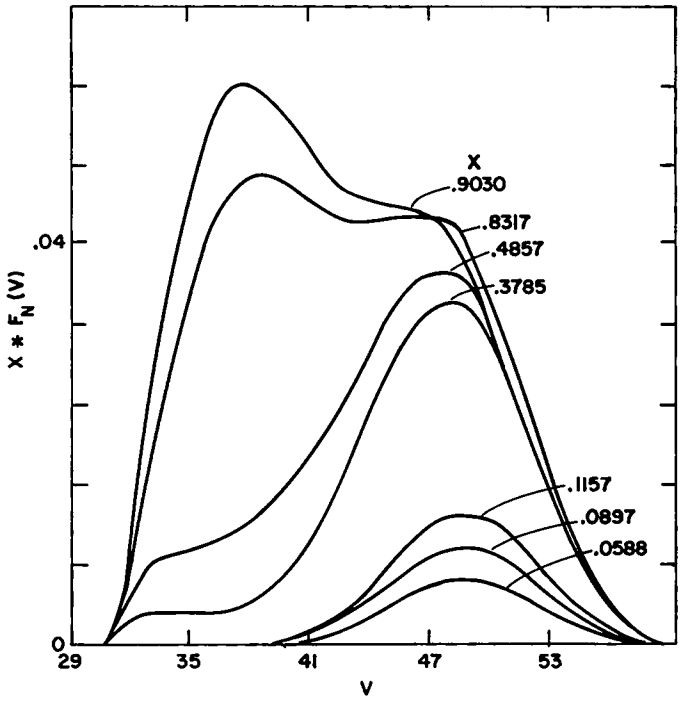

Fig. 10. Cumulative chromatograms at different conversions, 70°C, 0.3 wt-% AIBN.

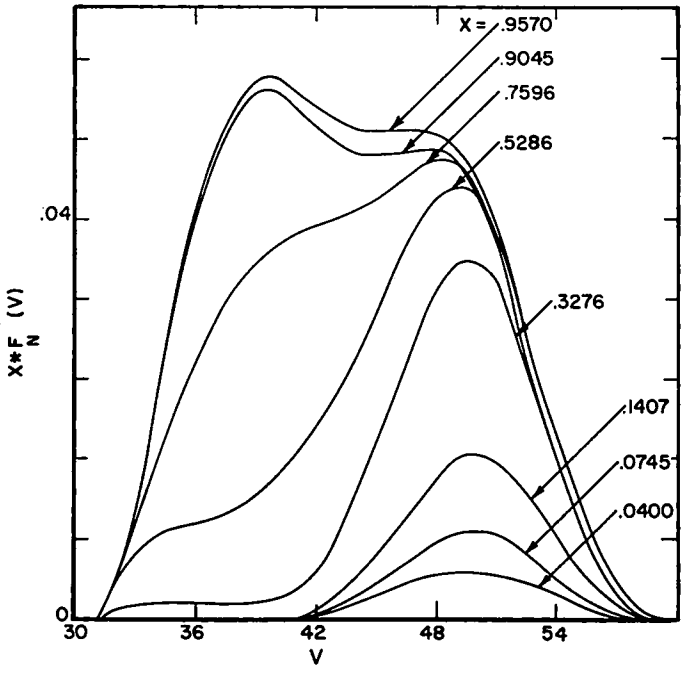

Fig. 11. Cumulative chromatograms at different conversions, 70°C, 0.5 wt-% AIBN.

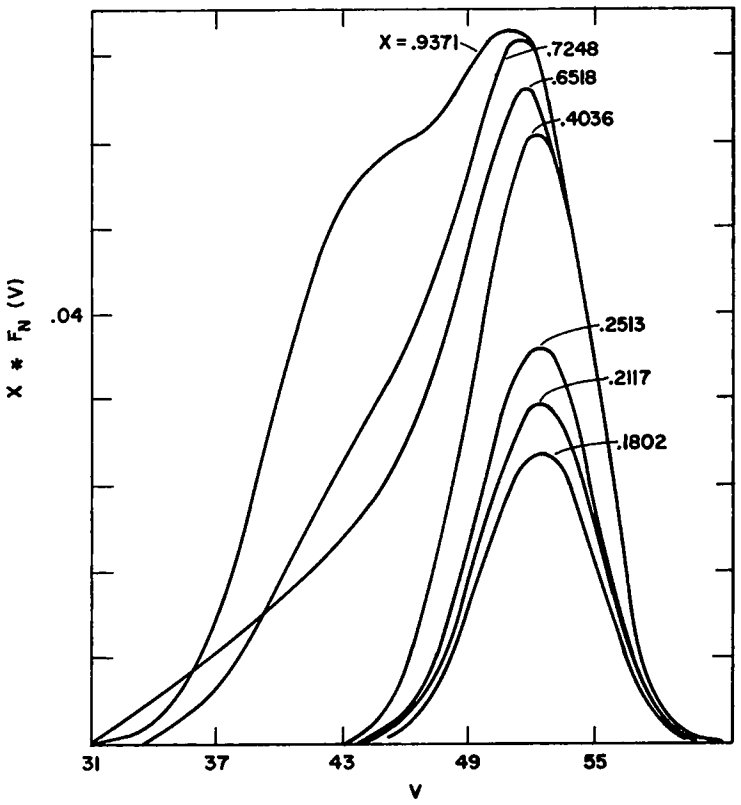

Fig. 12. Cumulative chromatograms at different conversions, 90°C, 0.3 wt-% AIBN.

DMWD's were measured by GPC. The instantaneous α_1 is located in the center of the horizontal bar. The instantaneous DMWD's found experimentally were in all cases most probable distributions. Values of α_1 found using the method of differential chromatograms were fit with two equations of the following form and later used as initial guesses for the method of chromatogram heights):

$$\text{Fit \#1:} \quad \alpha_1 = \exp(A + BX + CX^2) \tag{26}$$

$$\text{Fit \#2:} \quad \alpha_1 = \exp(A + BX + CX^2 + DX^3) \tag{27}$$

The parameters found are tabulated in Table XXVII. Typical chromatograms found using these functions, eqs. (26) and (27), are shown in Figures 16 and 17. Typical molecular weight averages derived therefrom are shown in Figure 7. PMMA obtained at 50°C had molecular weights beyond the resolution limit of our GPC columns. The chromatograms did, however, have similar shape to those found for the 70°C polymerization runs at high conversions.

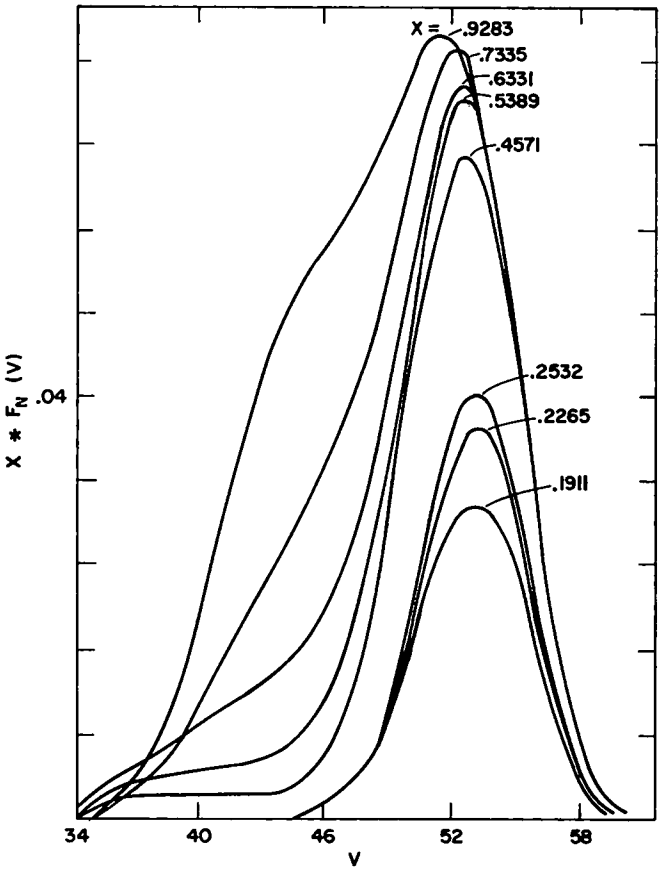

Fig. 13. Cumulative chromatograms at different conversions, 90°C, 0.5 wt-% AIBN.

In summary, the method of differential chromatograms gave good approximations to measured cumulative DMWD's over the whole conversion range, but more importantly provided instantaneous values of α_1. This immediately provided a reasonable functional form for the variation of α_1 with conversion and permitted the efficient use of the method of chromatogram heights.

The method of chromatogram heights was applied using eqs. (26) and (27) and values of the parameters found previously as the initial guess. The final values of the parameters are tabulated in Table XXVII. Typical α_1 values are plotted in Figure 15. This latter method generally gave better fits of both DMWD's and M_n and M_w values. (Refer to Fig. 7.)

Values of α over the conversion range were calculated using the best α_1 fits. You will recall that

$$\alpha = \frac{k_{td}}{k_p^2}\frac{R_p}{M^2} = \frac{1}{M_0}\frac{k_{td}}{k_p^2}\frac{dX}{dt}\frac{1+\epsilon X}{(1-X)^2} = \alpha_1\frac{(1+\epsilon X)}{(1-X)^2} \tag{28}$$

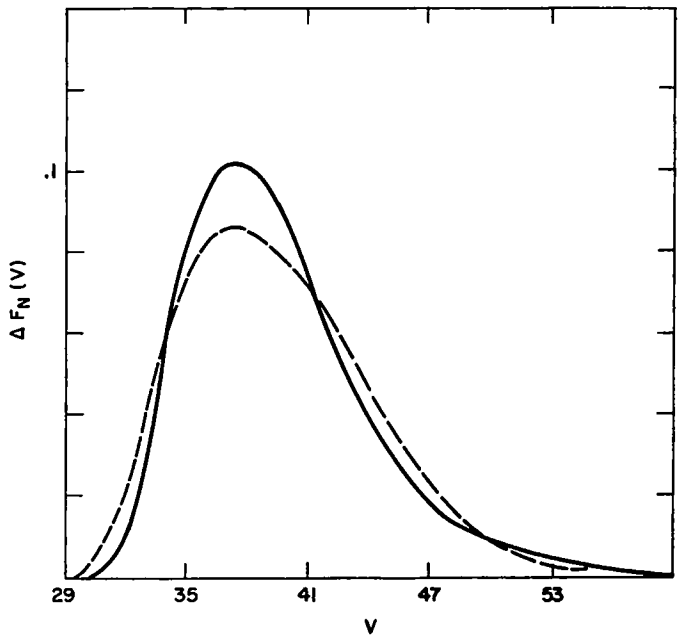

Fig. 14. Results of a single-variable search for α_1 using the method of differential chromatograms: (——) differential chromatogram from GPC nos. 589 and 595 (X = .4857 to .8317); (– – –) chromatogram from α_1 search.

TABLE XXVII
α_1 as a Function of Conversion[a]

Origin of function	Temp., °C	AIBN, wt-%	A	B	C	D
Fit #1 of α_1 from	70	0.3	−7.113	−4.39	−3.50	0
method of		0.5	−6.982	−3.44	−4.24	0
differential	90	0.3	−6.330	−2.23	−5.06	0
chromatograms		0.5	−6.108	−1.49	−6.07	0
Fit #2 of α_1 from	70	0.3	−7.214	−2.25	−10.23	5.17
method of		0.5	−7.125	−0.130	−15.13	8.73
differential	90	0.3	−6.434	0.180	−13.30	6.82
chromatograms		0.5	−6.245	2.49	−18.91	10.20
Search for B	70	0.3	−7.113	−4.35	−3.14	0
and C		0.5	−6.982	−2.98	5.27	0
	90	0.3	−6.330	−1.75	−6.66	0
		0.5	−6.108	−1.63	−6.36	0
Search for B,	70	0.3	−7.214	−1.77	−13.42	9.30
C, and D		0.5	−7.125	1.48	−22.67	15.32
	90	0.3	−6.434	−0.42	−10.34	2.69
		0.5	−6.245	2.13	−19.66	11.04

[a] $\alpha_1 = \exp(A + BX + CX^2 + DX^3)$.

TABLE XXVIII
Results of NMR Analyses

Kinetic sample no.	Reaction temp., °C	AIBN, wt-%	Conversion	i, %	h, %	s, %	σ
704H	50	0.391	.1449	3.0	29.9	67.0	.221
704C	50	0.391	.8413	2.4	32.8	64.7	.244
704B	50	0.391	.8601	2.1	32.2	67.2	.220
718J	70	0.5	.9570	3.4	34.6	62.0	.271
722D	90	0.5	.2531	3.0	34.8	62.0	.271
726D	90	0.5	.4602	2.2	34.2	63.5	.255
726F	90	0.5	.9663	3.3	37.2	59.5	.297

and that the instantaneous DMWD and molecular weight averages are a function of this single parameter. Typical α variations with conversion are shown in Figure 18, and these are compared with C_m. It is obvious that at no time during the polymerization does transfer to monomer influence molecular weights. It is also evident that from a conversion

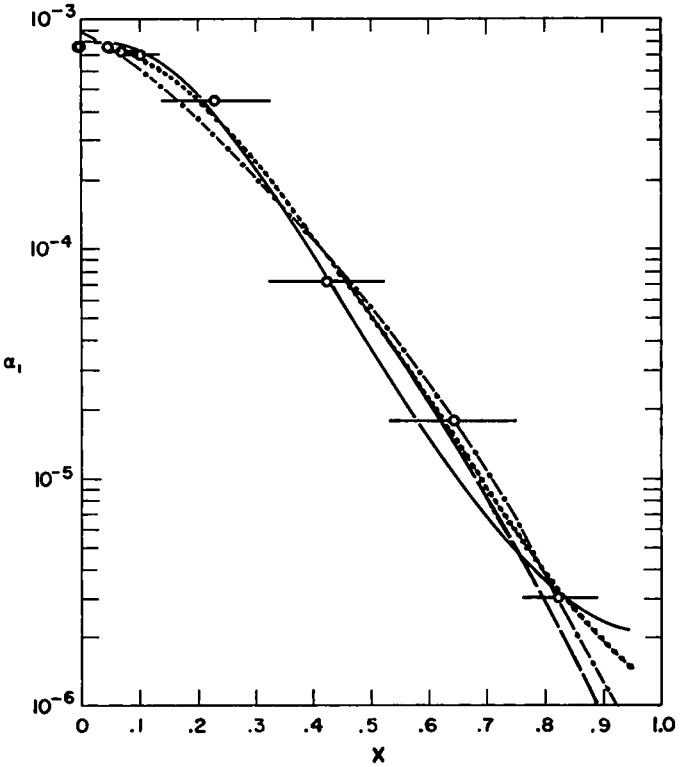

Fig. 15. α_1 vs. X, 70°C, 0.5 wt-% AIBN. α_1 from: (O) (—·—) fit #1 and (···) fit #2, method of differential chromatograms (ΔF_N); (— — —) 2-variable search and (——) 3-variable search, method of chromatogram heights.

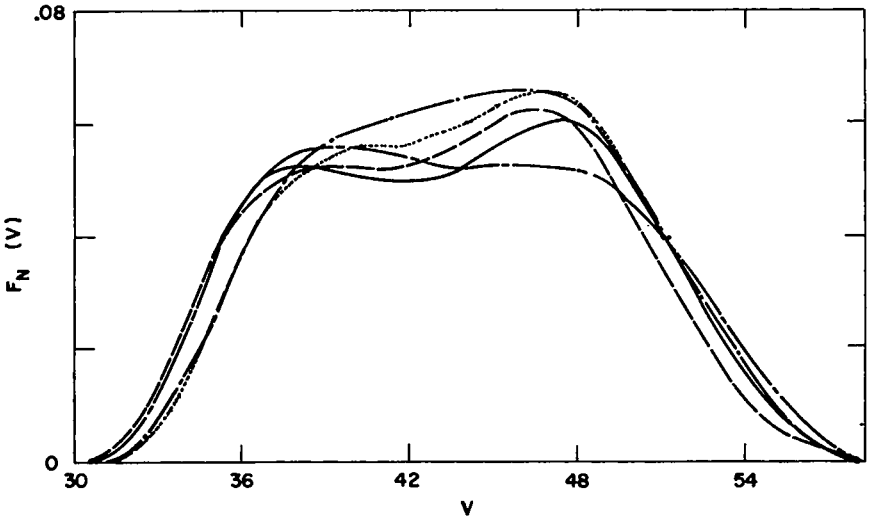

Fig. 16. Results of method of chromatogram heights on high-conversion sample (GPC no. 615) (X = .9570): (— — —) experimental chromatogram; (—·—) chromatogram using α_1 from fit #1; (– – – – –) chromatogram using α_1 from fit #2; (— — — —) chromatogram using α_1 from 2-variable search; (——) chromatogram using α_1 from 3-variable Search.

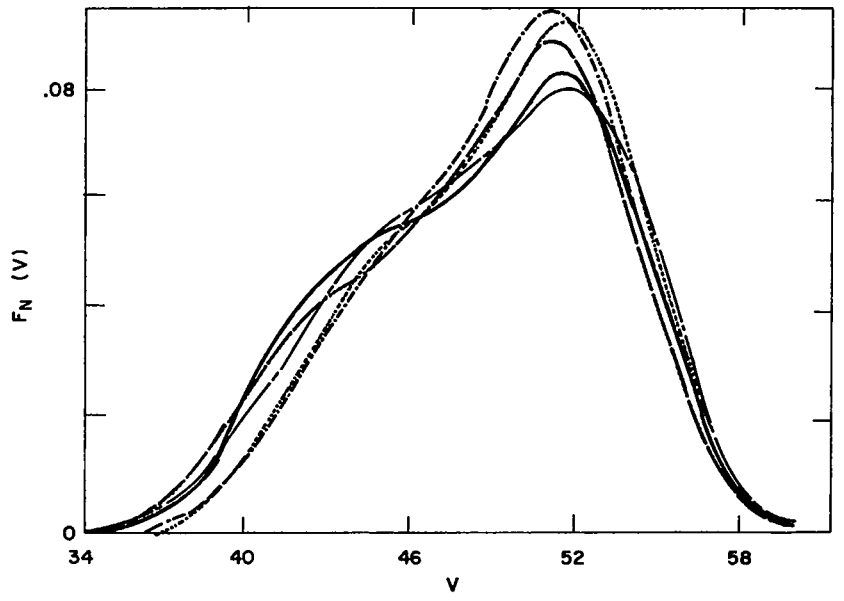

Fig. 17. Results of method of chromatogram heights on high-conversion sample (GPC no. 571) (X = .9283): (— — —) experimental chromatogram; (—·—) chromatogram using α_1 from fit #1; (· · ·) chromatogram using α_1 from fit #2; (— — — —) chromatogram using α_1 from 2-variable search; (——), chromatogram using α_1 from 3-variable search.

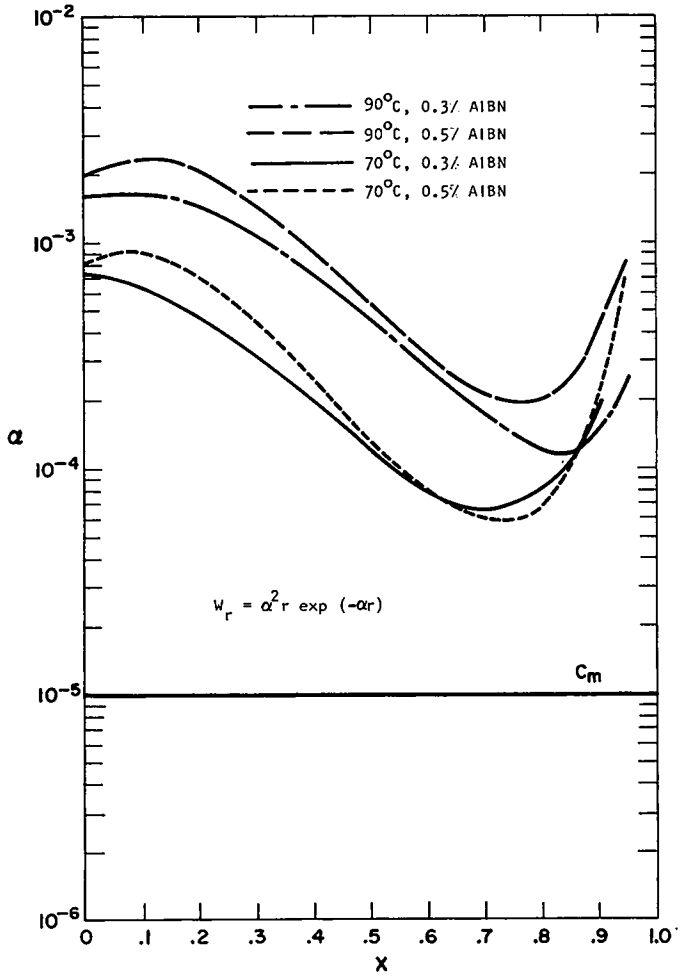

Fig. 18. $\alpha \left[= \alpha_1 \frac{(1 + \epsilon X)}{(1 - X)^2} \right]$ vs. X.

of about 80% on, the instantaneous molecular weights fall appreciably. Were transfer to polymer and/or terminal double bond polymerization important, one would expect an increase in molecular weights with conversion. This is clearly evident from the investigation of vinyl acetate polymerization by Graessley et al.[10] We cannot rule out the possibility that there is some transfer to polymer or terminal double-bond polymerization, however.

In summary, it has been shown that measured instantaneous DMWD's are most probable distributions and that therefore classical free-radical kinetics which hold at low conversions are also applicable during the gel effect when the termination reactions are diffusion controlled. The α_1 value decreases with conversion as k_{td} falls as a result of diffusion control.

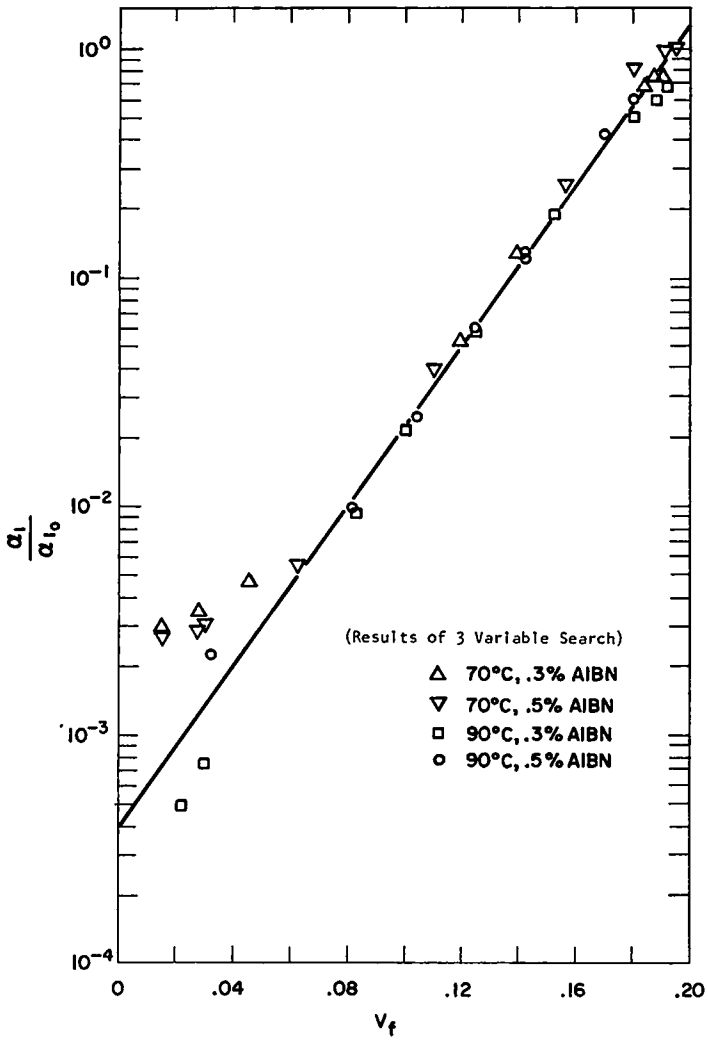

Fig. 19. $\frac{\alpha_1}{\alpha_{1_0}}$ vs. free volume for 70° and 90°C.

The increase in the rate of polymerization tempers the effect of the reduction of k_{td} on α_1, but not until after an initial high molecular weight spike forms. The model does not predict the growth of the spike well with the functions used for the variation of α_1 with conversion.

Gel Effect Correlation

In an attempt to find a general correlation for the effect of conversion on α_1 we investigated its variation with free volume. In particular, we plotted $\alpha_1/(\alpha_1)_{X=0}$ versus free volume V_f for all of the polymerizations at different temperatures, initiator levels, and conversions. These data are shown in Figure 19. The correlation is quite good down to a free volume of

about 0.05. This is equivalent to a conversion of about 75–80%. The scatter at lower free volumes may be due to a reduction in k_p which would have the effect of increasing the ratio $\alpha_1/(\alpha_1)_{X=0}$.

This general correlation could be used in the following manner. Let us suppose one wished to calculate the cumulative DMWD at 80°C for a conversion of 75% using 0.4 wt-% initiator. Firstly, calculate V_f as a function of conversion neglecting the effect of polymer molecular weight. Use the generalized plot (Fig. 19) and calculate $\alpha_1/(\alpha_1)_{X=0}$ as a function of conversion. The $(\alpha_1)_{X=0}$ value is already known from Figure 6 if dX/dt is known, and the calculation of the cumulative DMWD is a straightforward integration using eq. (23).

SUMMARY

It has been shown that during the gel effect the instantaneous DMWD is the most probable distribution suggesting that classical free-radical kinetics are equally applicable during diffusion control of termination.

Two new methods of determining kinetic parameters from experimental GPC data have been developed. These are "The Method of Differential Chromatograms" and "The Method of Chromatogram Heights." Both methods were used with MMA polymerization and were found to have merit.

A generalized correlation from which the effect of diffusion control on polymer molecular weight can be predicted a priori has been developed. It appears that the onset and magnitude of diffusion control of termination is closely connected to free volume.

Appendix

This appendix shows how the various GPC and kinetic model predicted chromatograms are calculated:

1 (*a*) *GPC Chromatogram, $F(v)$*

$F(v)$ = conventional raw chromatogram heights as a function of retention volume.

(*b*) *Predicted Chromatogram, $F(v)|_{\text{model}}$*

$$F(v)|_{\text{model}} = W_r|_{\text{cum}} \frac{dr}{dv} \int_{-\infty}^{\infty} F(v)dv$$

where

$$W_r|_{\text{cum}} = \frac{\int_0^X W_r dX}{X}.$$

The area under either $F(v)$ or $F(v)|_{\text{model}}$ is proportional to the weight of polymer injected into the GPC.

2 (*a*) *Normalized GPC Chromatogram, $F_N(v)$*

$$F_N(v) = \frac{F(v)}{\int_{-\infty}^{\infty} F(v)dv}.$$

(*b*) *Normalized Predicted Chromatogram,* $F_N(v)|_{\text{model}}$

$$F_N(v)|_{\text{model}} = W_r|_{\text{cum}} \frac{dr}{dv}.$$

The area under either $F_N(v)$ or $F_N(v)|_{\text{model}}$ is unity.

3 (*a*) *Cumulative GPC Chromatogram,* $F_C(v)$

$$F_C(v) = F_N(v) \cdot X.$$

(*b*) *Cumulative Predicted Chromatogram,* $F_C(v)|_{\text{model}}$

$$F_C(v)|_{\text{model}} = F_N(v)|\text{model} \cdot X.$$

The area under either $F_C(v)$ or $F_C(v)|_{\text{model}}$ is X.

4 (*a*) *Differential GPC Chromatogram*

$$\Delta F(v) = F_C(v)|_{X=X_2} - F_C(v)|_{X=X_1}.$$

(*b*) *Differential Predicted Chromatogram*

$$\Delta F(v)|_{\text{model}} = F_C(v)|_{\text{model},\ X=X_2} - F_C(v)|_{\text{model},\ X=X_1}.$$

The area under either $\Delta F(v)$ or $\Delta F(v)|_{\text{model}}$ is $X_2 - X_1$.

5 (*a*) *Normalized Differential GPC Chromatogram,* $\Delta F_N(v)$

$$\Delta F_N(v) = \frac{\Delta F(v)}{X_2 - X_1}.$$

(*b*) *Normalized Differential Predicted Chromatogram*

$$\Delta F_N(v)|_{\text{model}}$$

$$\Delta F_N(v)|_{\text{model}} = \frac{\Delta F(v)|_{\text{model}}}{X_2 - X_1}$$

$$= \frac{\left\{\int_0^{X_2} W_r dX - \int_0^{X_1} W_r dX\right\} \frac{dr}{dv}}{X_2 - X_1}$$

$$= \frac{\left\{\int_{X_1}^{X_2} W_r dX\right\} \frac{dv}{dr}}{X_2 - X_1}.$$

The area under either $\Delta F_N(v)$ or $\Delta F_N(v)|_{\text{model}}$ is unity.

In the method of chromatogram heights at low conversions, a single-variable Fibonacci search[12] is used with a single $F_N(v)$ to find α_1 which matches $F_N(v)|_{\text{model}}$ with $F_N(v)$. When high conversions are involved a series of $F_N(v)$ consecutive in time of reaction are matched simultaneously via a Nelder Mead simplex search[12] for α_1 as a function of conversion.

In the method of differential chromatograms, a Fibonacci search for α_1 is used to match $\Delta F_N(v)|_{\text{model}}$ with $\Delta F_N(v)$.

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