The spontaneous thermal polymerization of methyl methacrylate:
5*. Experimental study and computer simulation of the high conversion reaction at 130°C

Dedicated to Professor Dr. G. V. Schulz on the occasion of his 75th birthday

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The thermal polymerization and oligomerization of methyl methacrylate was studied at 130°C up to almost total monomer conversion. Using the rate constants for chain initiation and the diverse oligomerization steps given in our previous papers as well as literature values for chain propagation and termination, the kinetics of the complex reaction system was simulated with the computer program REMECH of DeTar. The good agreement between experimental and calculated concentration and molecular weight data indicates that the assumed reaction mechanism and the associated set of reaction constants are essentially correct.

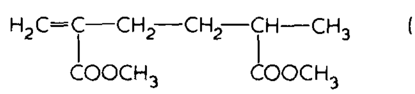
INTRODUCTION

It is now well established that methyl methacrylate (MMA), after thorough purification of the monomer and careful preparation of the reaction vessels, undergoes reproducible spontaneous thermal polymerization[2].

Even at relative high temperatures the thermal polymerization rates of MMA are very low, the rates of initiation being lower by a factor of about 10^7 than in the case of the thermal polymerization of styrene.

However, the molecular weights of the thermal polymers are extremely high and almost exclusively controlled by chain transfer reactions.

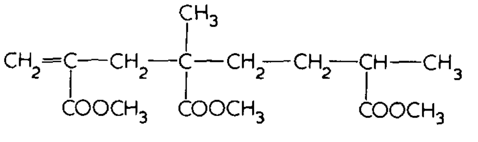
The spontaneous polymerization of MMA is accompanied by the production of several oligomers among which a linear unsaturated dimer H-1 (dimethyl 1-hexene-2,5-dicarboxylate) is predominant[3].



$H_2C{=}C(COOCH_3){-}CH_2{-}CH_2{-}CH(COOCH_3){-}CH_3$

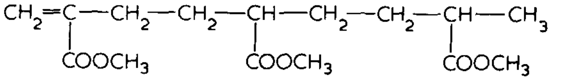
(H-1)

Just like the isolated and characterized trimers[1,4] O–1, N–1 and N–4 the dimer H-1 is formed in a second order side reaction[3,5,6] probably via a cyclic en-enophil transition state[1,7,8].



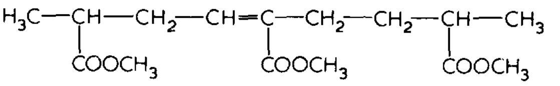
$CH_2{=}C(COOCH_3){-}CH_2{-}C(CH_3)(COOCH_3){-}CH_2{-}CH_2{-}CH(COOCH_3){-}CH_3$

(O-1)



$CH_2{=}C(COOCH_3){-}CH_2{-}CH_2{-}CH(COOCH_3){-}CH_2{-}CH_2{-}CH(COOCH_3){-}CH_3$

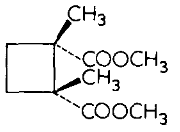
(N-1)



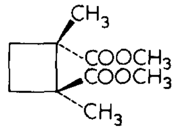
$H_3C{-}CH(COOCH_3){-}CH_2{-}CH{=}C(COOCH_3){-}CH_2{-}CH_2{-}CH(COOCH_3){-}CH_3$

(N-4)

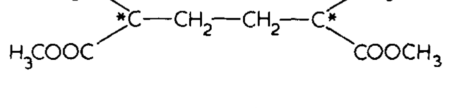
On the other hand it can be assumed that, according to the Woodward–Hoffmann rules[9], the isolated cyclic dimers cCB and tCB[1,4] are produced via a two step mechanism with a biradical** structure in the transition state[11] or as an intermediate[12].



(cCB)



(tCB)



(*M$_2$*)

On grounds of kinetic[1,4] and thermochemic–kinetic arguments[13,14] we believe that this biradical *M$_2$* is also involved in the initiation reaction of the thermal polymerization of MMA† (ref 16).

The experimental facts and theoretical considerations mentioned above can be summarized in the following schematic reaction pathways for the thermal oligomerization and polymerization of MMA (M = monomer)

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* Part 4 see ref 1

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** For a definition and problems related with the term 'biradical' see ref 10.

† One must assume that there exist different states of biradicals *M$_2$*: two singlet biradicals (*cis* and *trans* conformation) leading to the dimers cCB and tCB[4] and a triplet biradical producing — in a yet unknown way — monoradical species for the polymerization reaction[1,4,15].

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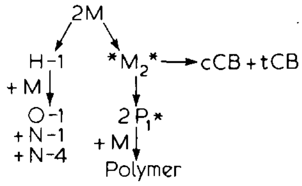
Table 1

No.	Reaction	Chemical equation	Reaction constant ($l\ mol^{-1}\ s^{-1}$)	Comments
1	Thermal initiation	$M + M \rightarrow 2P_1^*$	$k_i = 8.09 \times 10^{-16}$	(a)
2	Dimerizations	$M + M \rightarrow H{-}1$	$k_{H-1} = 7.53 \times 10^{-9}$	(b)
3		$M + M \rightarrow cCB$	$k_{cCB} = 1.86 \times 10^{-11}$	
4		$M + M \rightarrow tCB$	$k_{tCB} = 1.16 \times 10^{-11}$	
5	Trimerizations	$H{-}1 + M \rightarrow T$	$k_T = 4.17 \times 10^{-9}$	(c)
6	Chain propagation	$P_r^* + M \rightarrow P_{r+1}^*$	$k_p = 1.87 \times 10^3$	(d)
7	Chain transfer to monomer	$P_r^* + M \rightarrow P_r + P_1^*$	$k_{tr,M} = 0.117$	(e)
8	Chain transfer to H–1	$P_r^* + H{-}1 \rightarrow P_r + P_1^*$	$k_{tr,H-1} = 0.292$	
9	Chain transfer to trimers	$P_r^* + T \rightarrow P_r + P_1^*$	$k_{tr,T} = 0.409$	
10	Termination by combination	$P_r^* + P_s^* \rightarrow P_{r+s}$	$k_{tc} = 1.07 \times 10^7$	(f)
11	Termination by disproportionation	$P_r^* + P_s^* \rightarrow P_r + P_s$	$k_{td} = 2.74 \times 10^7$	



where it is further assumed that the primary radicals P_1^* are equally reactive. The aim of the present paper is to support this model by further experimental data as well as by computer simulations.

EXPERIMENTAL

The purification of the monomer, the preparation of the reaction setup, and details of the polymerization, were described earlier[2]; isolation and quantitative determination of the oligomers was done as described in ref 3.

To account for the considerable volume contraction during reaction all concentrations were corrected. Using previously given data for the density of monomer, H-1, trimers* and the apparent specific volume of the polymer[3] the following molar volume contraction values were estimated:

$$\Delta V_{\text{dimers}} = -32.6\ \text{cm}^3\ \text{mol}^{-1}$$
$$\Delta V_{\text{trimers}} = -69.4\ \text{cm}^3\ \text{mol}^{-1}$$
$$\Delta V_{\text{polymer}} = -35.3\ \text{cm}^3\ \text{base mol}^{-1}$$

Molecular weights were obtained by gel permeation chromatography with correction for axial dispersion according to Berger and Schulz[2,17].

COMPUTER SIMULATIONS

Computers have now gained widespread use in chemical kinetics. One of the most versatile programs for studying reaction mechanisms of any complexity is REMECH[18].

In the case of the thermal polymerization of styrene, REMECH has already proved to be a powerful tool for mechanistic studies[19]. REMECH accepts a reaction mechanism consisting of a set of chemical equations plus assigned values for all rate and equilibrium constants plus a set of initial concentrations. By numerical integration the program provides tables with concentration data of reactants, products, and intermediates as a function of reaction time. REMECH 'computes the theoretical curves about which the experimental data are supposed to fall if the mechanism and associated reaction constants are correct'[18]. In this sense 'REMECH does not replace techniques now in use for the study of reaction mechanisms, but rather supplements them'[18].

Table 1 lists the reaction steps and rate constants which we have assigned to the individual steps for the thermal oligomerization and polymerization of MMA.

Comments to Table 1

(a) As the detailed mechanism of the initiation of the thermal polymerization of MMA is still unknown, we write the initiation step in agreement with experimental results[4] as an overall second order reaction leading to two equally reactive monoradicals P_1^*. The rate constant k_i was calculated from the Arrhenius parameters of the initiation rate R_i given in ref 2.

(b) The rate constants for the dimerization reactions were estimated from the corresponding Arrhenius equations given earlier[1,3].

(c) The insufficient g.c. separation of the trimers (cf. picture 4 in ref 3) did not allow a separate determination of the concentrations of O-1, N-1 and N-4. Therefore the small amount of O-1 was neglected and T means the sum of N-1 and N-4. Accordingly, $k_T = k_{(N\text{-}1+N\text{-}4)}$ given in the preceeding paper[1].

(d) The rate constant for the chain propagation k_p was taken from the literature[20,21]. As compared with the monomer the homopolymerization of the unsaturated dimer H-1 is very slow[22] and was therefore neglected. The same holds for the unsaturated trimers.

(e) Because of the very low rates of initiation chain transfer reactions play a dominant role in controlling molecular weights during thermal polymerization of MMA. A simplified Mayo equation

$$\frac{1}{\bar{P}_n} = \frac{2}{\bar{P}_w} = \Sigma C_x \cdot \frac{[X]}{[\mathrm{M}]} \qquad (1)$$

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* The individual trimers could not be separated with the g.c.-technique used in [3]. Therefore in the following 'trimers' means the mixture of 0-1, N-1 and N-4, the nonen derivatives dominating 0-1 by far[1,3]. It was further assumed that the cyclobutane derivatives cCB and tCB have the same density as the linear dimer H-1

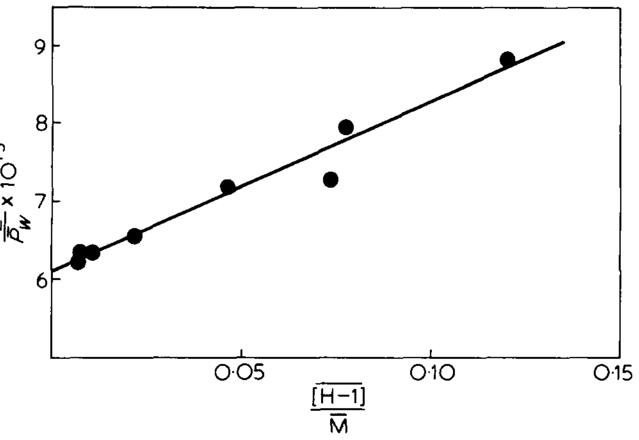


Figure 1 Estimation of the chain transfer constant C_{H-1} for the transfer reaction to the dimer H–1

can easily be derived[2] (X = chain transfer agent).

The rate constant $k_{tr,M}$ for the chain transfer to monomer was calculated according to $k_{tr,M} = C_M \cdot k_p$ with the (relative) chain transfer constant $C_M = 6.23 \times 10^{-5}$ given in a previous paper[2].

The rate constant $k_{tr,H\text{-}1}$ for the chain transfer to H-1 was estimated by plotting $2/\bar{\bar{P}}_w$ vs. $\overline{[H\text{-}1]}/\overline{[M]}$ where $\overline{[H\text{-}1]} = 0{,}5 \cdot [H\text{-}1]$ and $\overline{[M]} = 0.5([M]_0 + [M])$. In this way one can roughly take into account the changes in concentrations of dimer H-1 and monomer during the reaction. The plot (*Figure 1*) yields $C_M = 6.1 \times 10^{-5}$ in good agreement with the value above and $C_{H\text{-}1} = 2.2 \times 10^{-4}$. The latter numerical value was used as an initial guess for simulations with REMECH and was then further refined until good agreement between experimental and calculated molecular weight data was obtained (see below). This procedure led to $C_{H\text{-}1} = 1.56 \times 10^{-4}$ and $k_{tr,H\text{-}1} = 0.292$ given in *Table 1*. For the mixture of trimers it was assumed that $k_{tr,T} = k_{tr,M} + k_{tr,H\text{-}1}$. Transfer to the cyclic dimers cCB and tCB is of minor importance and was, therefore, neglected.

(f) The rate constants for disproportionation and combination at low conversions were taken from the literature[20,21]. It was assumed that the ratio of these two termination reaction modes remained unchanged throughout the whole conversion while the gel effect was accounted for by proper damping of k_{tc} and k_{td} (see below).

By using dummy products it is possible to calculate cumulative number-average degrees of polymerization $\bar{\bar{P}}_n$ with the aid of REMECH, too[18,19].

Counting the 'molar flow' of monomer through the chain propagation reaction (step 6 in *Table 1*) will provide the amount of monomer incorporated in polymer, $(n_M)_P$. However, one can add all moles of dead polymer n_P produced by termination and transfer reactions (steps 7–11 in *Table 1*).

Then
$$\bar{\bar{P}}_n = \frac{(n_M)_P}{n_P} \qquad (2)$$

The rate of polymerization is:

$$R_P = \frac{(n_M)_P}{t} \qquad (3)$$

(t = reaction time).

The cumulative weight-average degrees of polymerization $\bar{\bar{P}}_w$ can be estimated as follows[14]:

$\bar{\bar{P}}_w$ is related with $\bar{\bar{P}}_n$ by [23,24]

$$\bar{\bar{P}}_w = \bar{\bar{P}}(1+U) \qquad (4)$$

Furthermore for a Schulz-distribution the non-uniformity U can be substituted in equation (4) via[21,25]

$$1+U = \frac{(3-w_1)\cdot(1+w_1)}{2} = 2 - \frac{w_2{}^2}{2} \qquad (5)$$

through w_1 or w_2, the weight fractions of polymer chains with degree of coupling $k=1$ or $k=2$. w_1 can be expressed as

$$w_1 = \frac{\Sigma m_{tr} + m_{td}}{\Sigma m_{tr} + m_{td} + m_{tc}} = \frac{\Sigma n_{tr} + n_{td}}{\Sigma n_{tr} + n_{td} + 2n_{tc}} \qquad (6)$$

where Σm_{tr}, m_{td} and m_{tc} are the total weights of polymer molecules produced by chain transfer reactions, disproportionation, and combination. Σn_{tr}, n_{td} and n_{tc} are the corresponding mole numbers. The factor of 2 in $2n_{tc}$ arises because polymer molecules with degree of coupling $k=2$ have (on the average) twice the mass of those with $k=1$. Obviously,

$$n_P = \Sigma n_{tr} + n_{td} + n_{tc} \qquad (7)$$

therefore equation (6) can be rearranged to:

$$w_1 = \frac{n_P - n_{tc}}{n_P + n_{tc}} \qquad (8)$$

Similar considerations lead to:

$$w_2 = \frac{2n_{tc}}{n_P + n_{tc}} \qquad (9)$$

for the weight fraction of molecules with $k=2$.

Combining equations (4), (5) and (8) one can get $\bar{\bar{P}}_w$. The calculation of Σn_{tr}, n_{td}, and n_{tc} is facilitated by using 'RCT'-tables which display the integrated increments of reaction flow along the various paths[18].

As mentioned in the experimental section we corrected our analytical measurements for the considerable volume contraction during reaction. The same was done with REMECH calculations by using the 'EVEN INCREMENTS – Option'[18] taking reaction increments of 2% along reaction pathway 6 (chain propagation) and correcting the concentrations after each interval.

All calculations with REMECH were run on a DEC 10 computer using ~30 s CPU time for the whole simulation.

RESULTS AND DISCUSSION

Table 2 summarizes the experimentally determined concentrations of reactant and products as well as cumulative molecular weight averages for the thermal polymerization and oligomerization of MMA at 130°C with almost total monomer consumption.

Experiments in solution had shown that both polymeri-

Table 2

t (h)	[M]	[H−1]	[cCB]	[T]	[P] *	10^2x	$10^{-4}\bar{P}_w$	$10^{-4}\bar{\bar{P}}_n$	U
75	7.817	0.118	0.0003	0	0.157	4.79	3.16	1.56	1.03
270	7.204	0.334	0.0012	0.0034	0.473	13.83	3.06	1.64	0.87
530	6.213	0.655	0.0034	0.0595	0.884	27.71	2.79	1.28	1.18
745	5.400	0.991	0.0044	0.0588	1.203	38.48	2.75	1.34	1.05
1025	4.916	1.005	0.0045	0.0553	1.855	45.18	2.51	1.29	0.95
1270	3.851	1.428	0.0069	0.1030	2.148	58.10	2.30	1.05	1.19
1555	3.479	1.317	0.0075	0.1313	2.840	62.89	1.99	0.98	1.03
1891	2.691	1.353	0.0082	0.1627	3.745	72.15	1.87	0.89	1.10
2200	1.625	1.621	0.0100	0.1553	4.605	83.71	1.81	0.77	1.35
2729	0.658	1.730	0.0108	0.1555	5.688	93.62	1.71	0.66	1.59
3215	0.211	1.601	–	0.2283	6.440	98.00	1.54	0.55	1.80
3713	0.126	1.612	–	0.1568	6.776	98.81	1.50	0.43	2.49

* Base moles

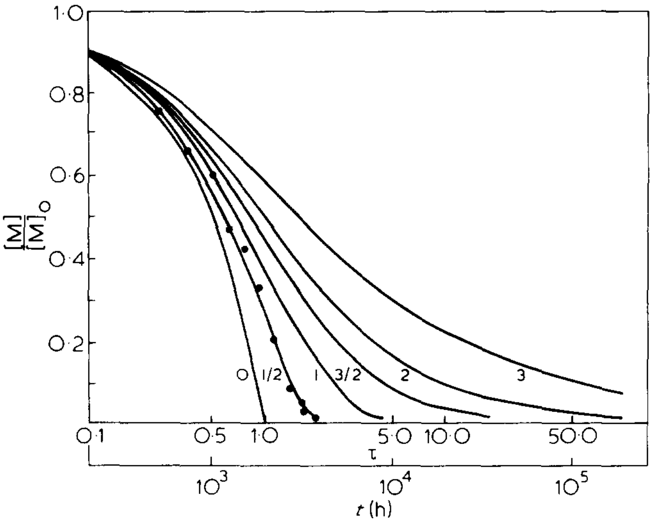


Figure 2 Powell plot for the overall monomer consumption (polymerization plus dimerization)

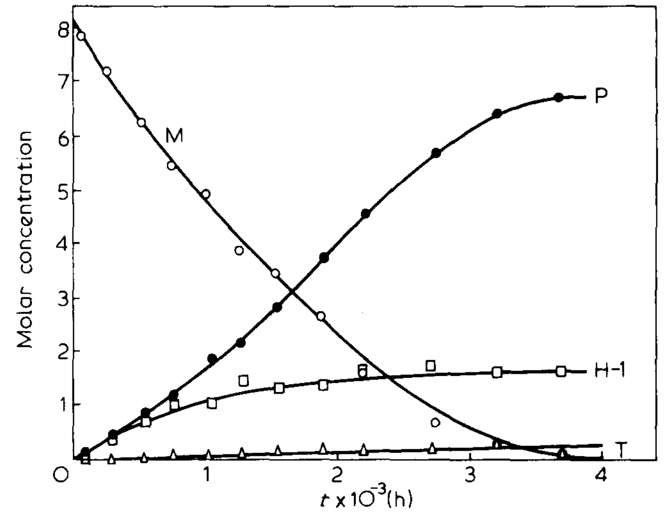


Figure 3 Experimental data and computed curves for the molar concentrations of reactant and products for the thermal polymerization and oligomerization of MMA at 130°C. M = monomer; H−1 = dimer H−1; T = mixture of the trimers N−1 and N−4; P = polymer (in base mole units)

zation and individual dimerizations were second order reactions with respect to the monomer concentration[3,4]. Neglecting the small amount of trimers the total monomer consumption should depend on $[M]^2$, too. The Powell plot[26] in *Figure 2* shows that this is not the case for the bulk reaction to high conversions. The observation that the apparent 'internal reaction order'[27] ($n_{\mathrm{int}}=1/2$) deviates from the results in solution and at low conversions ('external reaction order'[27] $n_{\mathrm{ext}}=2$) was also made with the thermal polymerization of styrene in the early experiments of G. V. Schulz and Husemann[28] who got $n_{\mathrm{int}}=1$ and $n_{\mathrm{ext}}=2$.

Two reasons can be given for this deviation. Firstly, the volume contraction was neglected in the Powell plot and secondly, the well known gel effect will lead to a continuously decreasing rate of termination, giving an apparent lower reaction order.

The complete quantitative description of high conversion polymerizations with gel effect is still an unsolved problem although recent work of O'Driscoll and coworkers[29] can be looked upon as a promising step in the right direction.

In our complex reaction mixture with high contents of oligomers this theory of O'Driscoll seems to be untractable. Therefore we made use of the computer program REMECH of DeTar and 'fitted the gel effect empirically'. *Figure 3* shows the result.

All rate constants given in *Table 1* except k_{tc} and k_{td} were held constant over the whole reaction. The termination rate constants k_{tc} and k_{td} were decreased continuously until good agreement between experimental and calculated polymer yield was obtained.

Figure 3 demonstrates that by this procedure our experimental data can be predicted very well with the assumed reaction mechanism and the assigned rate constants in *Table 1*. The (relative) decrease of k_{t} $(=k_{\mathrm{tc}}+k_{\mathrm{td}})$ by a factor of $\sim 10^5$ with increasing conversion

$$x=\frac{[M]_0\cdot V_0-[M]\cdot V}{[M]_0\cdot V_0} \tag{10}$$

as received from the simulations with REMECH is depicted in *Figure 4*. Nevertheless the gel effect is weak as seen from the relatively small increase in the radical concentration [P*] by a factor of about 10. Noteworthy is a flat minimum in the polymer radical concentration curve (at $x\sim 0.25$), the onset of gel effect as defined by O.Driscoll. Lissi and coworkers[30]. At conversions $x>0.95$ the termination rate constant falls off very steeply, while the radical concentration remains constant. Obviously at this stage of reaction the mobility of the macroradicals is frozen in.

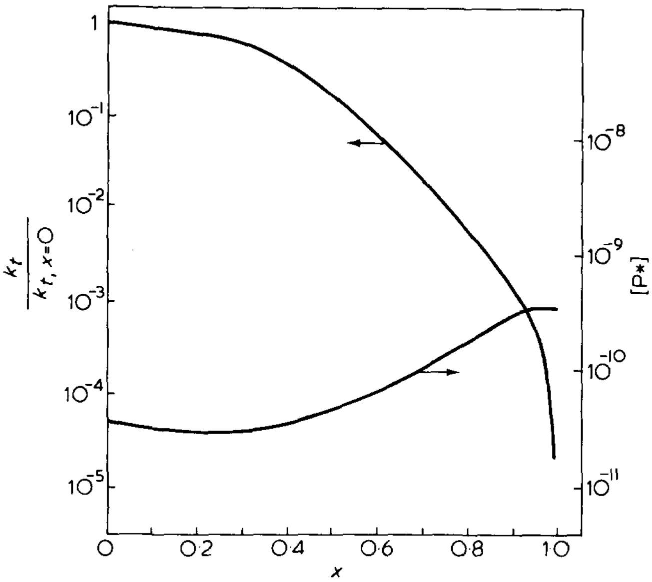


Figure 4 Simulated conversion dependencies of the chain termination constant k_t and the macroradical concentration [P*]

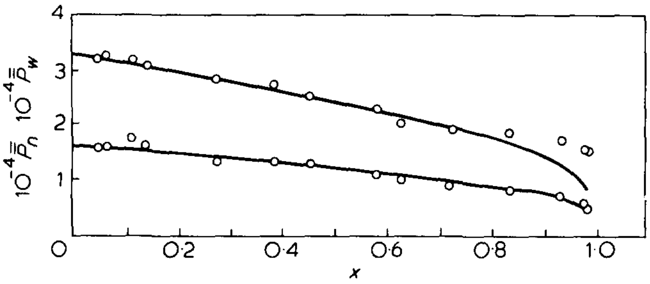


Figure 5 Experimental data and computed curves for the conversion dependencies of the cumulative average degrees of polymerization $\bar{\bar{P}}_n$ and $\bar{\bar{P}}_w$ during thermal polymerization of MMA at 130°

The computer simulations were run with a constant value for the chain propagation constant k_p throughout the whole course of reaction. We believe this assumption to be justified because, due to the high content of plastifying oligomers, the polymerizing system is always far from its glass transition temperature.

Figure 5 shows the experimental data and calculated curves for the dependences of the cumulative number- and weight-average degrees of polymerization on conversion. Up to ~80% conversion the agreement is quite good indicating that the values of the chain transfer constants $C_{H-1} = 1.56 \times 10^{-4}$ and $C_T = 2.2 \times 10^{-4}$ given implicitly in *Table 1* are reasonable. As compared with the monomer the higher value for the dimer H-1 is probably a consequence of the relatively loose bond of the H-atom attached to the tertiary C-atom in the latter compound[31]. But it should be held in mind that transfer constants to substrates with polymerizable double bonds are sometimes falsified by copolymerization[21].

Using labelled monomer we could show that at 60°C the AIBN-initiated copolymerization of MMA with H-1 takes place ($r_{MMA} = 1.8$, $r_{H-1} = 0.33$)[22]. However, i.r. measurements showed that the polymer formed during thermal polymerization at 130°C did not contain more than 5 mol percent H-1 units even at the highest conversions[14]. This problem should be studied further with refined analytical techniques (e.g. *FT*i.r.) in future work.

At conversions higher than ~80% the measured values of $\bar{\bar{P}}_w$ are systematically higher than predicted ones whereas the agreement in $\bar{\bar{P}}_n$ remains good. At the same time the non-uniformity rises from 1 to 2.5 (*Table 2*). We think this is a consequence of neglecting chain branching.

In principle two modes of chain branching can occur during the polymerization of MMA:

(a) branching at the double bond of a chain end formed by disproportionation[32] or transfer to a monomer molecule[33]. In this case higher $\bar{\bar{P}}_n$ values will result[33].

(b) branching by radical transfer to the polymer chain. This does not influence $\bar{\bar{P}}_n$ but results in higher $\bar{\bar{P}}_w$ values.

The latter case is observed in our experiments and can be rationalized with the extremely low concentration of end-groups in a polymer with such high molecular weights. In the thermal polymerization of MMA nearly all dead polymer molecules are formed by chain transfer reactions. *Figure 6* gives the conversion dependence of the fractional contributions of the different chain transfer reactions to the total production of polymer as computed with REMECH. In the whole range the contribution of disproportionation and combination termination is significantly lower than one percent, justifying the presumption made in deriving equation (1).

Although only present in spurious amounts the cyclic dimers cCB and tCB are very important byproducts of the thermal polymerization of MMA. Their presence strongly supports the assumption that biradicals $^*M_2^*$ are intermediates for the initiation reaction of the thermal polymerization of this monomer (see above).

Unfortunately the analytical techniques used in this work were not efficient enough for a good separation of the dimers cCB and tCB. We restricted ourselves to an estimation of the concentration of cCB. *Figure 7* shows the experimental results as well as computed curves for the concentrations of cCB and tCB. The reaction constants for the formation of these dimers used in our

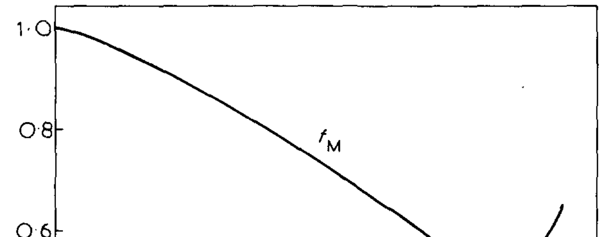


Figure 6 Conversion dependencies of the fractional contributions of the different chain transfer reactions to the production of dead polymer molecules (M = monomer; H–1 = Dimer H–1; T = mixture of trimers N–1 and N–4)

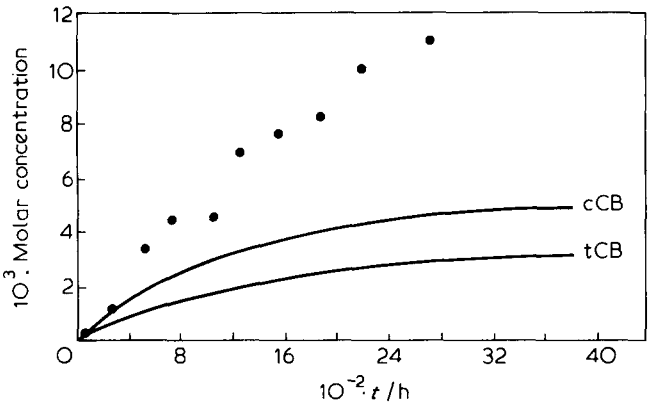
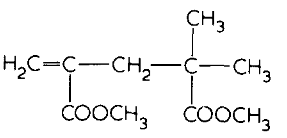


Figure 7 Computed concentration–reaction time curves for the dimers cCB and tCB. ● = experimental data for cCB

REMECH simulation are based on experiments at low conversions with improved g.c.-separation techniques[1] and are therefore reliable. That is why we assume that the experimental data for cCB obtained in the present study are falsified.

In our preceding paper[1] we reported about an additional dimer P-1



$$H_2C{=}C(COOCH_3){-}CH_2{-}C(CH_3)(COOCH_3){-}CH_3$$

(P-1)

which can be detected in very low concentrations in the dimer fraction of the reaction mixture and whose g.c.-separation from cCB and tCB is very difficult. The same compound was observed in PMMA solutions after prolonged standing at room temperature indicating a possible degradation of the polymer.

The assumption that the g.c. signal, assigned in the present work to the dimer cCB, can be attributed to the sum of cCB and the degradation product P-1, is supported by quite a good correlation between the difference Δ[cCB] of experimental and calculated cCB concentrations and the polymer content [P] (in base moles) of the reaction mixture (*Figure 8*).

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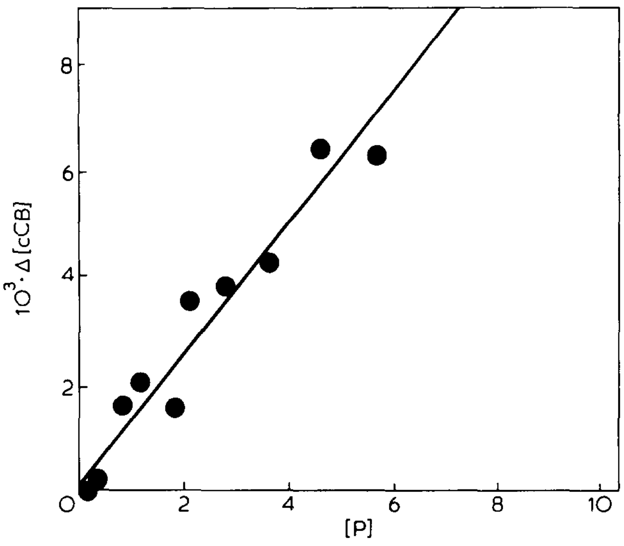

Figure 8 Correlation between the difference in calculated and measured concentration of cCB, Δ [cCB], and polymer concentration [P] (in base moles)

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