Macromolecules

Volume 21, Number 12 December 1988

Free Radical Polymerization of Methyl Methacrylate up to the Glassy State. Rates of Propagation and Termination[1a]

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ABSTRACT: The free radical polymerization of methyl methacrylate in bulk at 0 °C initiated by photochemical decay of azobis(cyclohexanenitrile) (ACN) is tested over the full range of conversion up to the glassy state. Rate constants of propagation, k_p, and termination, k_t, are evaluated by the rotating sector technique and after effect. Instantaneous degree of polymerization and efficiencies, f, are given for all conversions. The conversion dependence of f can be expressed by the self-diffusion of small molecules in a polymer matrix. Both rate constants depend on the conversion; k_t for conversions near and beyond the onset of entanglement also depends on the chain length of the polymer radicals but becomes independent of this length at about 45% conversion. The diffusion processes describing the different stages of conversion are discussed.

Introduction

The kinetic mechanism of vinyl polymerization by free radicals has been studied extensively, and there is vast literature on this subject. Most of the work in the past, however, has been restricted to the so-called ideal region of low conversion and to the determination of the ratio k_p^2/k_t and other parameters available from steady-state experiments.

More recently attention has been directed to theoretical and experimental studies in the more advanced stages of the polymerization process, and we started to obtain a more reasonable description of the Trommsdorff or gel effect of the reaction mixture by the measurement of absolute rate constants of propagation and termination, k_p and k_t, respectively, up to the glassy state.

The determination of absolute rate constants is a delicate experimental task. Only a limited amount of published data is available, and it is mostly restricted to the low conversion range. Thus it seemed worthwhile or even essential to study the influence of conversion on the propagation and termination rates under non-steady-state conditions in spite of the difficulties to be expected.

The experiments had to be done on a polymer which was well characterized and preferably had a low transfer coefficient, for these reasons methyl methacrylate was chosen as the test monomer. In order to get low rates of polymerization and negligible thermally initiated polymerization, the experiments were carried out in bulk at 0 °C using 1,1′-azobis(1-cyclohexanenitrile) (ACN) as the initiator, which decays almost exclusively by a photochemical process at this temperature.

The low-temperature polymerizations have the advantage of providing well-defined initiation of the kinetic chains and a relatively easy method of determining the k_p^2/k_t ratio, but the high molecular weight polymer chains in the reaction are a disadvantage because of the difficulties in measuring number- and weight-average degrees of polymerization.

Experimental Section

For the determination of the ratio k_p/k_t in the low-conversion range, intermittent illumination of the reaction by a rotating sector was used. For the more advanced and high-conversion regimes the post effect was measured as the decrease of the polymerization rate after illumination had been stopped and thus generation of ACN radicals had been stopped. The two techniques can be applied in different conversion ranges only. There is no conversion for which both could be used with sufficient accuracy.

The non-steady-state experiments were evaluated together with classical steady-state polymerizations yielding fk_p^2/k_t. The efficiency f was determined from $\bar{P}_n$ and $U = \bar{P}_w/\bar{P}_n - 1$. The number-average degree of polymerization $\bar{P}_n$ and the nonuniformity U were obtained from size-exclusion chromatography (GPC or SEC) on styrene gel (Waters and TSK) and controlled pore glass (Rhône-Poulenc) columns in tetrahydrofuran at 25 °C using refractive index and UV-absorption detectors to measure the concentration. Our high molecular weights made an application of membrane osmometry impossible.

The reaction mixtures were sealed in poly(ethylene terephthalate) (PET) bags and placed in an osmometer like device consisting of two quartz windows joined to a capillary which was filled with a water–methanol mixture. The fall of the meniscus in the capillary allowed the evaluation of the polymerization rate R_p.

We are well aware that the use of PET bags for the polymerization rather than an all glass apparatus and high vacuum slightly decreases the experimental accuracy. There was an induction period observed, and often the R_p slightly decreased in

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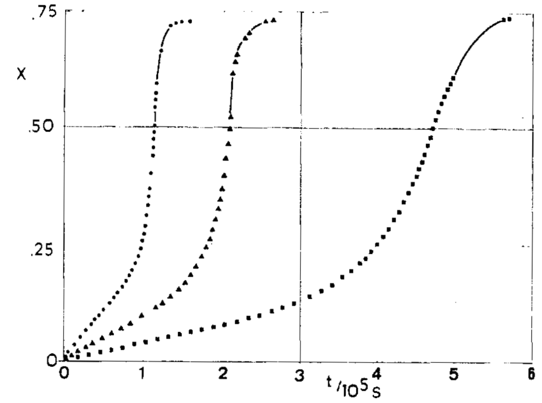

Figure 1. Polymerization of methyl methacrylate at 0 °C. Conversion x versus time for (●) $[I]_0 = 6.4 \times 10^{-3}$ mol L^{-1}, (▲) $[I]_0 = 1.6 \times 10^{-3}$ mol L^{-1}, and (■) $[I]_0 = 0.4 \times 10^{-3}$ mol L^{-1}.

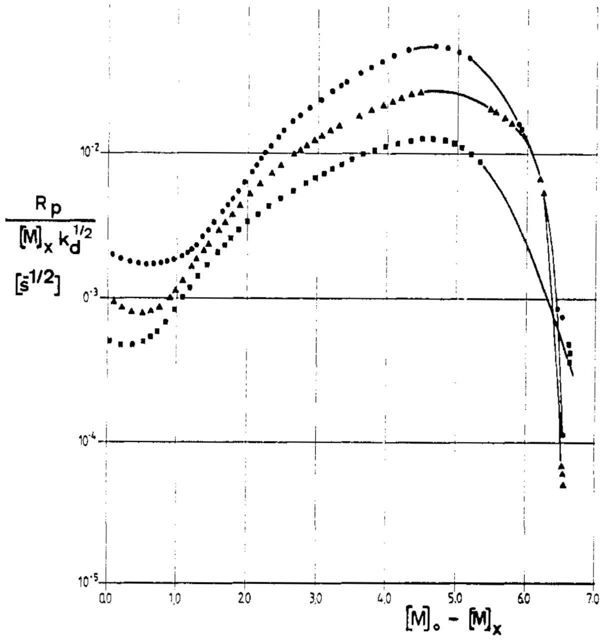

Figure 2. Overall rate of polymerization reduced for consumption of monomer and variation of k_d as a function of conversion. Compare Figure 1.

the low conversion range for experiments run in PET bags, but a decrease of R_p in the $0 \leq x \leq 0.05$ conversion range has also been reported for experiments run in very clean glass surrounding.

Therefore the induction period is the main disadvantage caused by the use of PET bags for the high conversion volume contraction experiments. But this effect period is the easily be corrected.

A more detailed description of the experimental techniques can be found in the thesis[1a] and a forthcoming paper.[1b]

Results

Figure 1 represents the increase of conversion x with time t for three initiator concentrations, $[I]_0 = 6.4 \times 10^{-3}$, 1.6×10^{-3}, 0.4×10^{-3} (mol L^{-1}). The rate of polymerization is rapid until the conversion reaches 0.73. At this point the overall rate of polymerization becomes extremely slow, due to the fact that the polymer–monomer mixture has reached the glassy state at the low reaction temperature of 0 °C.

In Figure 2, the ratio $R_p/[M]_x k_d^{1/2}$ is shown as a function of $[M]_0 - [M]_x$, where k_d is the rate constant for the decay of initiator ACN and $[M]_x$ is the monomer concentration at conversion x. The plot takes into account the decreasing monomer concentrations and via different k_d the different light intensities of the UV lamps (Osram HBO 500) for the different experiments.

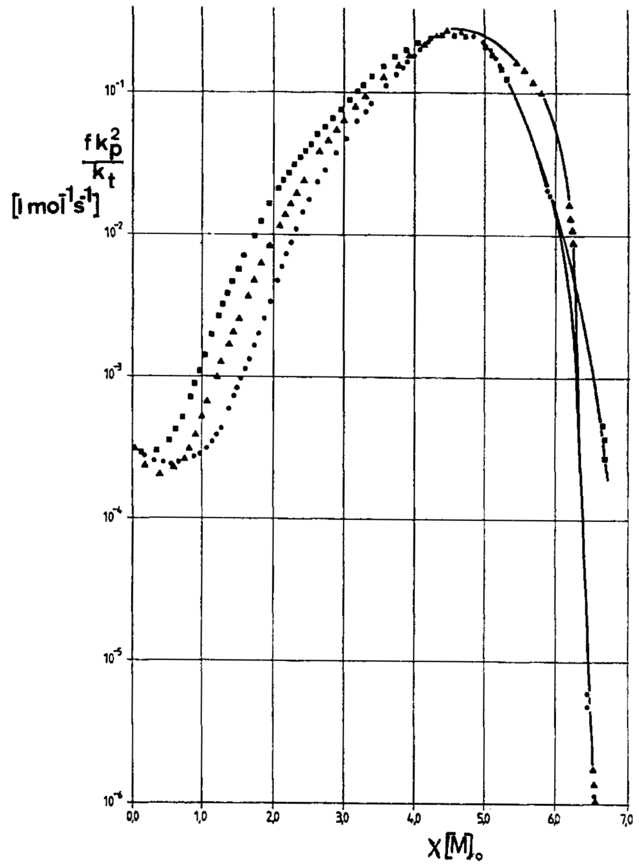

Figure 3. Characteristic ratio fk_p^2/k_t as a function of conversion. Compare Figure 1.

From the relation

$$R_p = \left(\frac{2fk_dk_p^2}{k_t}\right)^{1/2}[I]^{1/2}[M]_x \qquad (1)$$

the characteristic ratio

$$\frac{fk_p^2}{k_t} = \frac{R_p^2}{[M]_x^2}\,\frac{1}{2k_d[I]} \qquad (2)$$

results, which is to be seen in Figure 3, representing plots of fk_p^2/k_t versus $[M]_0 - [M]_x$ for the three initiator concentrations used here.

The evaluation of gel chromatographic and light-scattering experiments resulted in cumulative number- and weight-average degrees of polymerization $\bar{\bar{P}}_n$ and $\bar{\bar{P}}_w$. Figure 4 shows the cumulative number-average degrees of polymerization for the three initiator concentrations ([I] normalized for constant k_d) as full lines.

The cumulative values of the degrees of polymerization are converted to the instantaneous values according to Schulz[2] by the relationships

$$\bar{P}_n = \bar{\bar{P}}_n\left(1 + \frac{x}{\bar{\bar{P}}_n}\,\frac{d\bar{\bar{P}}_n}{dx}\right)^{-1}; \qquad \bar{\bar{P}}_w + \frac{d\bar{\bar{P}}_w}{dx} \qquad (3)$$

Figures 4 and 5 represent the instantaneous $\bar{P}_n$ and $\bar{P}_w$ values as a function of conversion which are of course appreciably higher than the cumulative values due to the strong increase of chain length with increasing conversion.

The efficiency f, the kinetically effective fraction of the initiator radicals formed, can be calculated from

$$f = \frac{2}{2 - w_2}\,\frac{R_p}{2\bar{P}_n k_d[I]_x} \qquad (4)$$

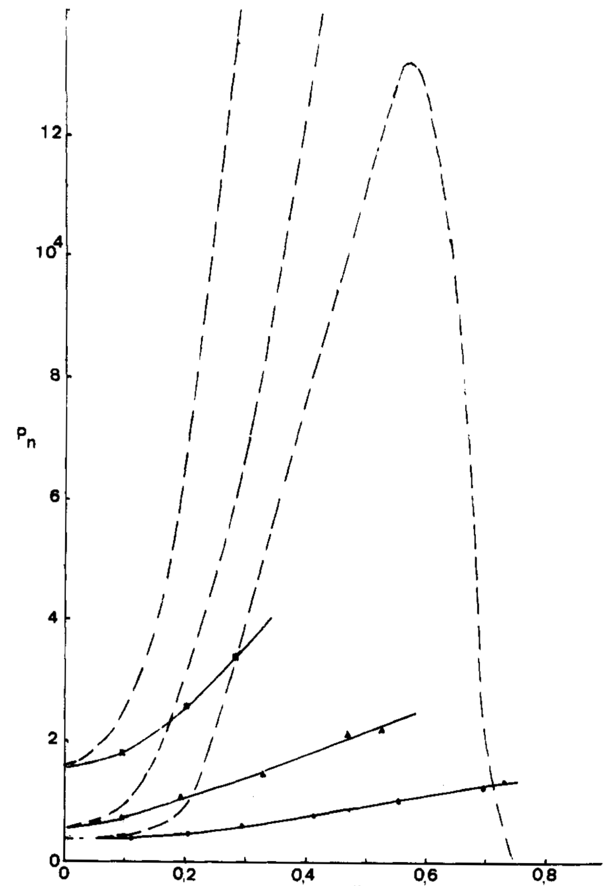

Figure 4. Cumulative number-average degree of polymerization, $\bar{P}_n$ (—), and instantaneous number-average degree of polymerization, $\bar{P}_n$ (- - -), as a function of conversion x.

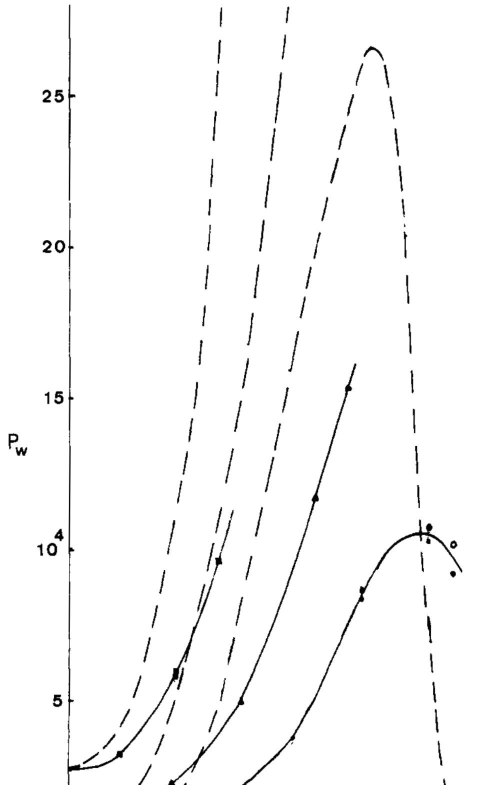

Figure 5. Cumulative and instantaneous weight-average degrees of polymerization, $\bar{P}_w$ and $\bar{P}_w$, as a function of conversion x.

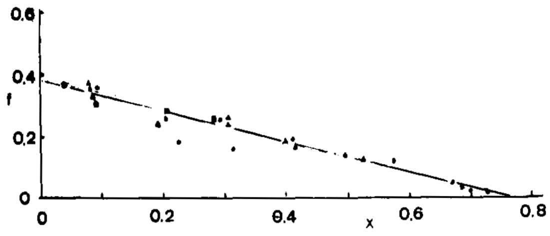

Figure 6. Experimental data for the efficiency f versus conversion x at 0 °C.

where w_2 is the fraction of two-chain polymers resulting from termination by combination in a mixed termination of combination and disproportionation. w_2 results from the nonuniformity as

$$w_2 = (2 - 2U)^{1/2} = \left(4 - 2\frac{\bar{P}_w}{\bar{P}_n}\right)^{1/2} \tag{5}$$

The results of our determinations are shown in Figure 6. The efficiency, within experimental accuracy, is shown to be a linear function of conversion with $f = 0.386$ for $x = 0$ and can be described by the equation

$$f = 0.386(1 - 1.31x) \tag{6}$$

The linearity of the concentration dependence of f up to the highest possible conversion is somewhat unexpected. The determination of the $\bar{P}_n$ values which are needed for eq 4 and 5 is quite difficult because of the high molecular weight of the polymers. For the two lower initiator concentrations only a crude estimation was possible.

Therefore it is necessary to test whether this behavior is plausible taking into account the constants k_{sep} and k_{rec} as well as the conversion dependence of k_{sep} in the definition relation of f:

$$f = \frac{k_{sep}}{k_{sep} + k_{rec}} \tag{7}$$

with k_{sep} the rate of separation of the initiator into a pair of radicals after decay and k_{rec} the rate of recombination of the same pair to an inert product. The rate of separation depends on the mobility of the radical and monomer molecule. The radical and monomer are supposed to be of comparable size and to have a comparable self-diffusion coefficient. In this case k_{sep} is proportional to $D_s = D_{self}$ and eq 7 becomes

$$f = \frac{D_s}{D_s + k'_{rec}} \tag{8}$$

where k'_{rec} is the corresponding coefficient for the recombination of the radical pair. There are no measurements of D for ACN radicals in our monomer–polymer system. But spin–echo determinations of similarly sized methyl ethyl ketone with added poly(methyl methacrylate) at concentrations up to 75% at 19 °C by Hwang and Cohen[3] can be used. The experimental results from samples with molecular weights between 10^5 and 5×10^5 are shown in Figure 7a. From the values $f_0 = 0.386$ and $D_{s0} = 3.11 \times 10^{-5}$ at zero concentration k'_{rec} is calculated as 4.99×10^{-5}, and this should be independent of the presence of polymer molecules and thus of the conversion. By inserting the experimental D_s of Figure 7a in eq 8, $f = f(x)$ is calculated and displayed in Figure 7b. From this figure it can clearly be seen that the f values calculated from D_s of methyl ethyl ketone at 19 °C are quite similar to our f values in Figure 6 at 0 °C. In fact, the efficiencies derived from the D_s function give an even better linear approximation than our

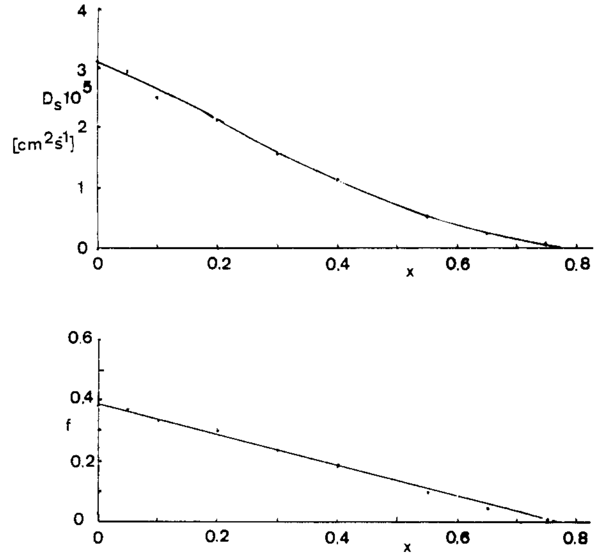

Figure 7. (a, Top) Self-diffusion coefficients D_s of methyl ethyl ketone in poly(methyl methacrylate) at 19 °C versus x, data from Hwang and Cohen.[3] (b, Bottom) Efficiency f calculated from $D_s = f(x)$ as above by using eq 8.

own data. Determination of self-diffusion coefficients of acetone and benzene in poly(methyl methacrylate) of $\bar{M}_w = 1.8 \times 10^5$ and $U \approx 1$ by Kosfeld and Schlegel[4] also allow one to calculate the concentration dependence of the efficiency. Again a good linearity is observed, the slopes for acetone at 20 °C and methyl ethyl ketone at 19 °C are about identical. For benzene at 20 °C and acetone at 0 °C the slope is somewhat larger, the constant in eq 6 changes from 1.31 to about 1.6. In any case, a good linearity for the conversion dependence results. The experiments of Kosfeld and Schlegel[4] are shown in Figure 12 in another context.

For the evaluation of experiments applying the rotating sector technique or the observation of the post effect, a stationary or at least a quasi-stationary state for small increments of conversion has to be accepted. The derived ratios k_p/k_t are plotted in Figure 8 for the three initiator concentrations.

From k_p/k_t and k_p^2/k_t the single rate constants are obtained. The experimental error of the constants is the same for k_p and k_t: ±8% for the rotating sector and ± 12% for the post effect. The behavior of k_p versus conversion is demonstrated in Figure 9a neglecting the different initiator concentrations. There seems to be a jump between the points observed by the rotating sector ($x < 0.1$) and those from observation of the post effect for the bulk polymerization of methyl methacrylate at 0 °C.

Figure 9a also shows the approximation of all measured k_p values by a horizontal with k_p = const = 135 up to $x = 0.65 - 0.70$ followed by a strong decrease as Schulz[5] proposed. The horizontal corresponds to a purely chemical control of the propagation reaction lasting until the glass point. The average k_p value of 135 includes between $x = 0$ and $x = 0.6$ k_p values from 80 to 230 which is a rough approximation. Thus we have to replace Figure 9a by a plot distinguishing between the different initiator concentrations used here, which is shown in Figure 9b.

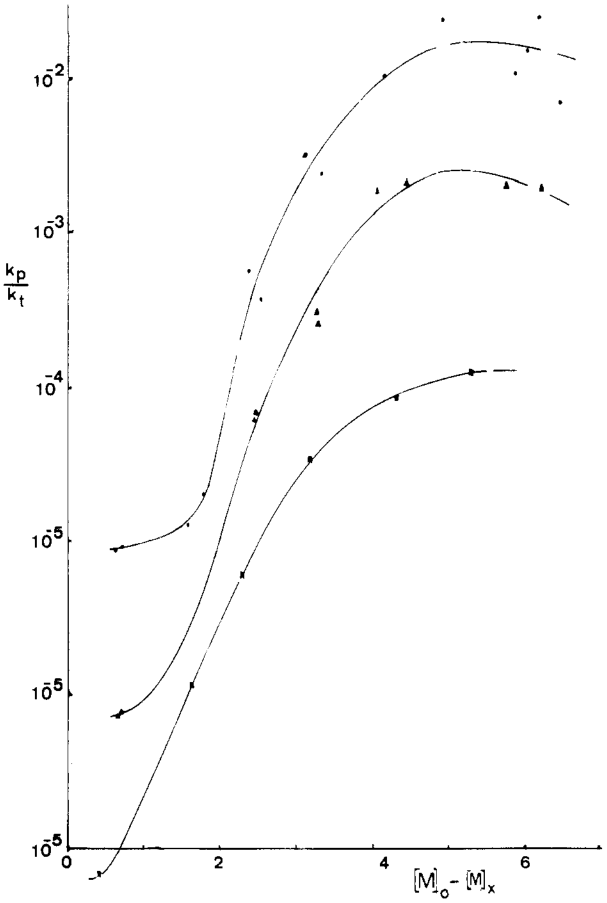

Figure 8. Ratio k_p/k_t as a function of conversion x for $[I]_0$ as in Figure 1.

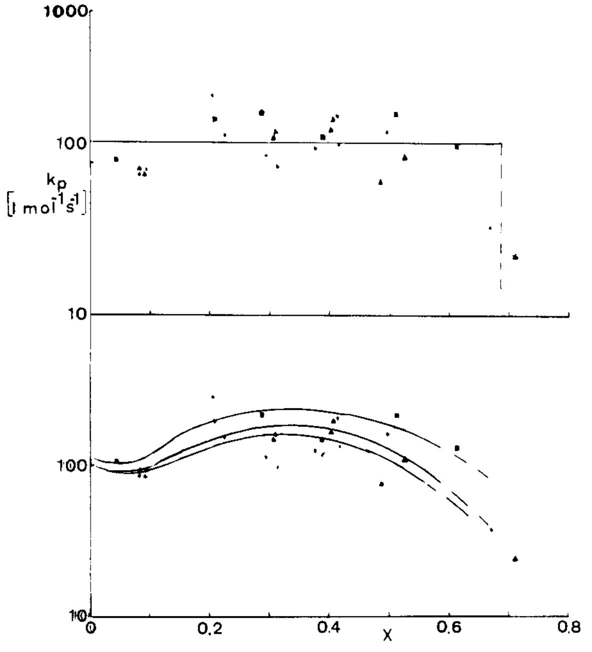

Figure 9. (a, Top) Rate constant of propagation, k_p, for all three initiator concentrations as a function of conversion x represented by an average value $k_p = 135$, $x < 0.1$ from the rotating sector; $x > 0.1$ from the after effect. (b, Bottom) Same experimental points as above differentiating between the different initiator concentrations from the top to the bottom curve: (■) $[I]_0 = 0.4 \times 10^{-3}$ mol L^{-1}; (▲) $[I]_0 = 1.6 \times 10^{-3}$ mol L^{-1}; (●) $[I]_0 = 6.4 \times 10^{-3}$ mol L^{-1}.

Both parts a and b of Figure 9 show a decreasing k_p starting at about $x = 0.35$. This indicates that there should be a conversion-dependent effect changing the control type from purely chemical to diffusional for the addition of monomers to the growing chain. Authors using the free volume theory in order to describe the conversion dependence of k_p (compare, e.g., Stickler[11]) accept an early influence of the translational diffusion coefficient of the monomer upon the propagation rate. The qualitative behavior of k_p as a function of conversion of our experi-

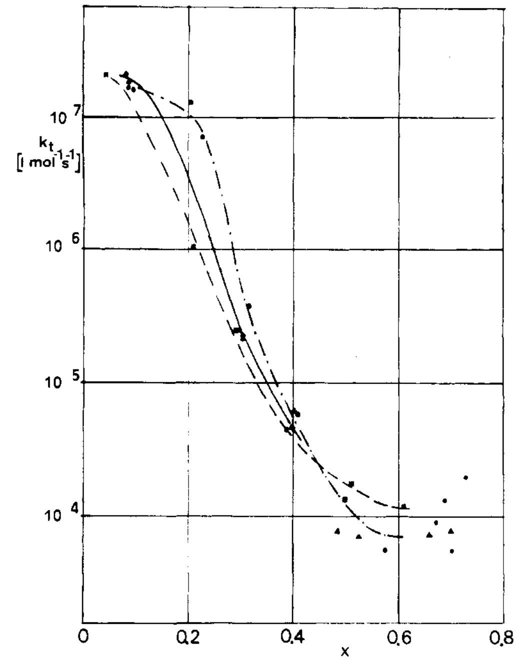

Figure 10. Rate constants of termination as a function of conversion x for the initiator concentrations of Figure 1.

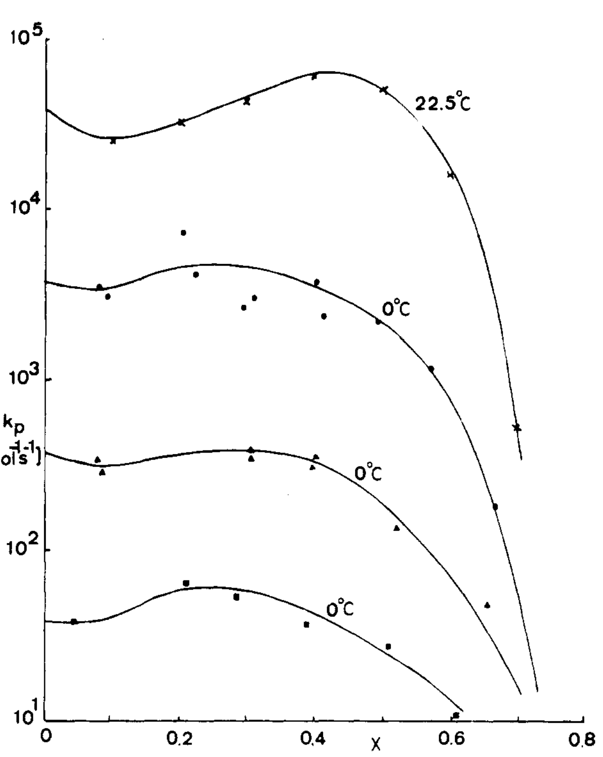

Figure 11. Products fk_p from Hayden and Melville[7] for poly(methyl methacrylate) at 22.5 °C and from this work at 0 °C with initiation rates: 22.5 °C (×) $R_i = 2.8 \times 10^{-8}$ mol L^{-1} s^{-1}; 0 °C (●) $R_i = 1.0 \times 10^{-8}$, (▲) 2.1×10^{-9}, (■) 3.5×10^{-10} mol L^{-1} s^{-1}.

ments shows a decrease after passing a maximum far below the glass point. The steepness of the decrease strongly increases toward the glass point. This phenomenon has been expected to be connected with the self-diffusion coefficient of translation of the monomer and is shown here for the first time by experimental k_p values from nonsteady-state measurements.

Figure 9b can be interpreted by a nearly constant k_p value at zero conversion for all three initiator concentrations. k_p falls slightly or stays constant until about the critical entanglement concentration and then starts to rise to a weak maximum after which it decreases with increasing steepness toward the glass point. Despite an appreciable scatter of k_p especially at the highest initiator concentration, we may draw three different curves for the different initiator concentrations. The highest maximum belongs to the lowest [I] value and thus to the highest degrees of polymerization. For the medium and the lowest maximum we can accept lower degrees of polymerization. So a weak dependence on the chain length of k_p for higher conversions seems possible.

Figure 10 represents the conversion dependence on the termination rate constant for the three different initiator concentrations. The pronounced decrease of k_t with conversion is well-known. Some years ago a chain-length-dependent termination rate has been reported by Mahabadi and O'Driscoll[6] for methyl methacrylate and styrene polymerizations. Our measurement method is not sensitive enough to demonstrate whether a molecular weight dependence occurs for k_t at low conversions. This effect should be more pronounced for low molecular weights. Our $\bar{P}_n$ values mostly are higher than 4000 and could show only a small further decrease of k_t. For higher conversions ($x > 0.1$) k_t clearly depends on the initiator concentration and thus the chain length. At low [I] the degree of polymerization decreases with increasing [I], and for x = constant it follows quite closely the classical relation

$$\bar{P}_n \propto [I]^{-1/2}(k_p/k_t^{1/2})_{x=0} \qquad (9)$$

The conversion influences on k_p and k_t seem to partly compensate each other. The rate of termination for low conversions could be constant at only a few percentages of conversion. The termination rate then starts to decrease, runs through an inflection point, and then tends to a nearly constant value as the conversion approaches the glass point of the reacting system. The termination rate constants in the beginning and close to the glassy state when the conversion approaches 0.73 differ by a factor of about 10^4.

To the best of our knowledge these are the first experiments of absolute rate measurements for radical polymerizations proceeding to very high conversions since Hayden and Melville[7] who evaluated k_p and k_t for methyl methacrylate at 22.5 °C from measurements of the heat of polymerization. Their rate constants show similar behavior, as can be seen for k_p from Figure 11. The rate constant of propagation first runs through a minimum, then through a maximum, and finally decreases with increasing steepness. Hayden and Melville[7] did not attempt to determine the efficiencies. Therefore their k_p actually corresponds to fk_p, and we use Hayden and Melville's fk_p, corrected for monomer consumption for comparison with our fk_p values in Figure 11. In this figure fk_p versus conversion is plotted for initiation rates of 1.0×10^{-8}, 2.1×10^{-9}, and 3.5×10^{-10} mol/L^{-1} s^{-1} at 0 °C along with Hayden and Melville's fk_p values for an initiation rate of 2.8×10^{-8} mol/L^{-1} s^{-1} at 22.5 °C.

The curvatures for the plots of fk_p versus conversion for the two different determination methods are qualitatively the same although the minimum and maximum at 22.5 °C are more pronounced than for the 0 °C experiments. This may be caused by the temperature difference.

For our experiments there is a possibility of a discontinuity due to the change from rotating sector to after effect techniques at about $x = 0.1$. At 22.5 °C the complete range was measured by the same method, and there is no physical indication for a jump rather than a continual change in the dependence. Obviously, the scatter of the three lower curves in Figure 11 is much less than that of the averaging horizontal in Figure 9a.

Tirrell[8] reported k_t determinations for methyl methacrylate at 60 °C with added amounts of poly(methyl methacrylate) without giving details of the method used. Four polymer samples ($9 \times 10^4 \leq \bar{M}_w \leq 7 \times 10^5$) and concentrations well below the glass point of the system ($0.08 < c < 0.6$ g cm^{-3}) was measured. In this regime k_t decreased from 5×10^{-7} by about 2 orders of magnitude. At fixed c, an average decrease of k_t with increasing molecular weight appeared. The qualitative behavior of k_t as a function of concentration corresponds to our findings far below the glass point.

Discussion of the Chain Length as a Function of Conversion. The degree of polymerization generated at a conversion x is constant only for the very first part of the polymerization process for $\bar{P}_n$ and $\bar{P}_w$. At the temperature of 0 °C even this is valid only for the highest initiator concentration used ($[I] = 6.4 \times 10^{-3}$ mol L^{-1}). For the two lower initiator concentrations and the correspondingly higher chain lengths both $\bar{P}$ values seem to increase from the very beginning ($x = 0$). With the onset of entanglement due to the Trommsdorff effect, the increase of the degrees of polymerization becomes very pronounced. With further increasing conversion, surprisingly both $\bar{P}_n$ and $\bar{P}_w$ start to decrease again from a maximum at about $x = 0.57$ for the high [I], which is far below the glass point at $x = 0.73$ (see Figures 4 and 5).

For the lower initiator concentrations the chain lengths become too high ($\bar{P}_w > 3 \times 10^5$) for the determination of the molecular weights by GPC. We except a more pronounced decrease of the $\bar{P}_n$ values as compared with that of the high initiator concentration. Even at the high initiator concentration the nonuniformity, $U = \bar{M}_w/\bar{M}_n - 1$, could be determined with only a somewhat lower accuracy and resulted in $U \approx 1$ for $x > 0.5$. It appears to be reasonable to accept the same U value of about 1 or slightly higher also for the low initiator concentrations.

In physical terms the decrease of $\bar{P}_n$ and $\bar{P}_w$ could be described as resulting from the termination between to radical chains, the lengths of which are diminishing again near the glass point. Up to the maximum degree of polymerization, the average length of the two reacting chains grows and is about the same. With decreasing monomer content first one of the polymer radicals will become shorter and then both until finally only oligomer and primary radicals terminate.

Of course, proof of the presence of oligomers in the polymer sample cannot be given here. When isolating the polymers from the reaction mixture the oligomers are removed together with residual monomer and initiator molecules.

Discussion of the Conversion Dependence of k_p. The rate of propagation during radical polymerization is chemically determined as long as there are monomer molecules readily available for the radical chain ends of the growing polymers. This will be true for the first stages of polymerization, but diffusion control of monomer will take over far below the onset of the glass effect as conversion increases. The mobility of the monomer is then the essential parameter which may be expressed as the translational self-diffusion coefficient of the monomer in the matrix of dead and growing polymer chains of the reacting system. We will discuss this behavior in detail for three stages of polymerization.

Initial Stages of Conversion and k_p. For our experiments, the overall rate of polymerization, R_p, and the rate constant of propagation, k_p, showed a slight decrease for low conversions. The decrease of R_p could also result from an increase of the termination rate constant for low x as reported by Fischer.[9] In any case, the slight decrease in R_p and k_p is followed by a slowly accelerating increase of both, starting at or below the point of entanglement of polymer chains. This is in contrast with the accepted theory[10] that the increase of R_p with conversion results only from the restriction in mobility of the growing radicals. But after thoroughly correcting for the consumption of monomer and initiator and taking into account the decrease of efficiency with conversion, the occurrence of a slight minimum of k_p at low conversion is just outside the experimental error for our rate measurements and more distinctly outside the error for the heat measurements of Hayden and Melville.[7]

Intermediate Stages of Conversion and k_p. With the onset of entanglement a distinct increase of the rate of polymerization is observed resulting from a diffusion hindrance for the termination reaction. Because of the increasing viscosity of the reaction mixture, two radical chain ends need more and more time to come close enough to react. The self-diffusion of the end segments of the polymer radicals should govern this process and results in the well-known increase of the chain length.

Though the increase of R_p results mainly from the decrease of k_t, there is a possible minor contribution from an increase of k_p. This is shown by our experiments at 0 °C and more pronounced by the experiments of Hayden and Melville[7] at 22.5 °C. It is difficult to interpret this behavior physically.

For the main part of the intermediate conversion, k_p is nearly constant or shows a weak and broad maximum at 0 °C and a more pronounced maximum from the heat experiments at 22.5 °C.

Later Stages of Conversion and k_p. After passing the maximum, k_p decreases more and more rapidly with conversion and finally approaches the glassy state when the reaction system consists mainly of dead polymer chains, some polymer radicals, and some monomer. R_p then becomes extremely slow. During the last stages of conversion the remaining mobility of the monomer should govern the chain propagation. This mobility is represented by the self-diffusion coefficient of the monomer in the reaction mixture.

No determinations of self-diffusion coefficients D_s for methyl methacrylate in its polymer are known. But the self-diffusion coefficients of benzene and acetone of Kosfeld and Schlegel[4] and methyl ethyl ketone of Hwang and Cohen[3] in poly(methyl methacrylate) allow a qualitative comparison with the monomer methyl methacrylate. Figure 12 shows these self-diffusion coefficients versus conversion, and D_s of methyl methacrylate should fit into these curves. But there seems to be dependence on the molecular weight of the polymer matrix, in which D_s is measured. The polymers in Figures 9 and 11 have higher molecular weights than the $\bar{M}_w = 2 \times 10^5$ of the diffusion experiments. In Figure 11, $\bar{M}_w$ increase from the upper most to the lowest curve roughly as 1:2:4:8.

Since the measurements of self-diffusion cover only a restricted range of conversion and show a dependence on the solvent, it seems worthwhile to calculate D_s/D_{s0} for methyl methacrylate in poly(methyl methacrylate) from the free volume theory, e.g., by the method of Stickler.[11] The results for 0 and 20 °C are shown in Figure 12 as broken lines which decrease somewhat more rapidly with conversion than the D_s curves and thus represent a slightly better description of $k_p = f(x)$. In any case, the change from chemically controlled to diffusion controlled propagation runs over a broad range of conversion starting far below the glass point.

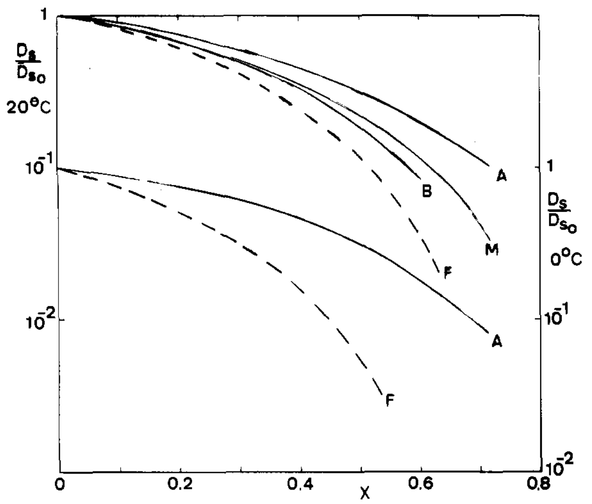

Figure 12. Self-diffusion coefficients D_s/D_{so} of (B) benzene,[4] (A) acetone,[4] and (M) methyl ethyl ketone[3] in polymethacrylate as a function of x = polymer content. $k_p/k_{po} = D_s/D_{so}$ as calculated from the free volume theory (F)[11] for comparison. Upper curves for 20 °C; lower curves for 0 °C.

In the general behavior of the propagation rate constant the observed slight increase at lower conversion is rather unexpected although the experiments of Hayden and Melville[7] show the same effect. While the increase of R_p with the onset of gel formation is well understood as the Trommsdorff[10] effect resulting from a hindered termination reaction, now a slightly growing propagation constant seems likely to also contribute to the increase of R_p with conversion.

Discussion of the Conversion Dependence of k_t. It is well-known that the termination rate decreases with increasing conversion. Generally the termination reaction of radical polymerization can take place only if two radical chain ends of growing polymers have a spatially close encounter. In dilute solutions during the first stage of conversion, an unhindered translational self-diffusion and a segmental or rotational diffusion of the chain ends occur simultaneously. It is reasonable to take the translational movement as the more rapid process, which means that the segmental diffusion determines the termination rate at low conversion. The behavior should change when the conversion is high enough for entanglements, which results in a strong decrease of the translational mobility. Thus for higher conversion, the translational self-diffusion will govern the termination rate.

The translational self-diffusion coefficient can be determined by measurements of forced Rayleigh scattering. At vanishing concentration the self-diffusion coefficient and the mutual-diffusion coefficient D_m are identical and of the order of magnitude 10^{-7} cm^2 s^{-1} for polymers in solution. D_m increases slowly with increasing concentration in a good solvent and always decreases with the molecular weight of the polymer. On the other hand, D_s strongly decreases with increasing conversion and molecular weight.[12] For example: polystyrene of $\bar{M}_w = 2 \times 10^6$ at $x = 0.1$ has a self-diffusion coefficient about 4 orders of magnitude lower than at $x = 0$.[13] For poly(methyl methacrylate) a similar strong decrease of D_s starting at $x = 0$ is to be expected. The behavior of k_t differs from that of D_s as can be seen in Figure 10 which shows k_t versus x for poly(methyl methacrylate) of a comparable molecular weight. There is only a small change in k_t for $x < 0.1$, larger changes in k_t as for D_s occur for higher conversions only. This means that for a comparison between the termination constant and D_s, the D_s values have to be shifted to higher conversions.

The mutual diffusion coefficient can be determined by dynamic light scattering in the fast mode.[12] For higher concentrations a second mode, the slow mode, can be measured.[3] The two modes are identical for low x and start to deviate at the critical entanglement concentration. Then the slow mode decreases quite rapidly, e.g., for poly(methyl methacrylate) with $\bar{M}_w = 3 \times 10^5$ the slow D_m decreases from 2×10^{-7} at about the critical entanglement concentration ($x \approx 0.08$) to about 10^{-13} at $x \approx 0.4$. This behavior shows similarity with k_t in Figure 10, but k_t decreases in this conversion range only by about 3 orders of magnitude.

Concerning the segmental diffusion coefficient, there is scarcely any direct experimental evidence, with the exception of the ESR measurements of Buchachenko and Wassermann,[14] of poly(vinylpyrrolidone) in ethyl alcohol at 20 °C that reports local translational diffusion coefficients versus polymer concentration up to 40 wt %. These diffusion coefficients are comparable with the k_t values of Hayden and Melville[7] for poly(methyl methacrylate) in methyl methacrylate at 22.5 °C where a simultaneous decrease of the segmental diffusion coefficient of poly(vinylpyrrolidone) and the termination rate constant of poly(methyl methacrylate) is found. The plot of $-\log D_{\text{segm}}{}^2$ versus $\log k_t$ (Figure 9 in ref 14) indeed shows a good similarity of two curves in which k_t of methyl methacrylate seems to have been corrected for comparison with that of poly(vinylpyrrolidone) in ethyl alcohol. Then, between the nearly constant D_{segm} at low concentration and D_{segm} at about 40% of weight of polymer, a decrease of an order of magnitude is observed. In the same concentration range the corrected k_t of methyl methacrylate changes about 1.8 orders of magnitude. The difference of about 0.8 orders of magnitude is too much and could perhaps be diminished by direct determinations of D_{segm} for poly(methyl methacrylate). Nevertheless, the type of segmental diffusion determined by Buchachenko and Wassermann[14] seems to be the best possible description of the conversion dependence of the termination rate constant at this time.

Conclusions

Since the basic paper of G. V. Schulz[5] there have been further attempts to describe the termination reaction of radical polymerization as a diffusional process[9,15,16] for all conversions. Certainly the net movement of two radical chain ends toward each other, due to all the possible diffusion processes, must govern this reaction. At the start of polymerization the diffusion takes place in dilute solution and asymptotically changes to a reptational movement of the chain ends carrying radicals through the increasing concentration of dead polymers.[17]

For low conversion a slight increase or a nearly constant value is observed for k_t below the onset of chain entanglements. The same behavior is observed for the mutual diffusion coefficient of polymers, D_m, which can be expressed as follows:

$$D_m = D_{mo}(1 + k_{d(M)}c)$$

$$D_m = K_{D(M)}M^{-\nu}(1 + k_{D(c)}M^{\mu}c) \qquad (10)$$

The two relations describe the concentration dependence of D_m in the dilute regime ($k_{d(M)}$ is a constant for each sample) and in the semidilute and concentrated regime, respectively. In the latter the constants are for polystyrene in toluene at 20 °C[13] $K_{D(M)} = 3.32 \times 10^{-4}$, $\nu = 0.574$, $k_{D(c)} = 3.6 \times 10^{-3}$ mL g^{-1}, and $\mu = 0.77$. The constants are given for polystyrene since mutual diffusion coefficients of comparable accuracy are not available for poly(methyl methacrylate). Toluene is a good solvent for polystyrene as is methyl methacrylate for poly(methyl methacrylate). In good solvents and at low concentration, D_m always increases with concentration, whereas it decreases in a θ solvent.

In a good solvent, D_m shows a similar behavior as k_t for the lowest conversion range. For higher concentration the scaling concepts[17] predict for a good solvent a further increase with concentration corresponding to $D_m \propto c^{0.75}$ and experiments prove this effect for polystyrene.[18] This is just the opposite behavior to the decrease of k_t with increasing conversion. A description of the decrease is given qualitatively by the slow mode of D_m.[3]

The decrease of k_t for somewhat higher conversions also conforms to the decrease of the self-diffusion coefficient D_s of polymers which starts to decrease at zero conversion. This means a representation of k_t is possible if the D_s values are shifted to higher concentrations.

The self-translational diffusion can be determined from gradient experiments with labeled polymers, but the reported data of Park[19] covered only a restricted concentration range. The newer forced Rayleigh scattering technique reports a decrease of D_s with increasing molecular weight and concentration.[11] The basic behavior of D_s for more concentrated solutions can again be described by the reptation model[17] as $D_s \propto M^{-2}c^{-1.75}$ and is in qualitative agreement with experiments on polystyrene.

Since D_m and D_s are the same for vanishing concentration, a combination of D_m for low x with D_s shifted to higher x values will result in diffusion coefficients turning from proportional to $M^{-\nu}$ to M^{-2}. For this case Tirrell et al.[8] presented an interpolation formula needing only an additional constant but leaving the problem of the necessary shift of D_s to higher concentrations unanswered. The function required for this purpose is still unknown. This shows once more the need for more experimental k_p and k_t determinations as a function of conversion, running to the highest possible conversions.

In order to describe the conversion dependence of k_t by a translational diffusion coefficient of the polymer molecules, some kind of empirical adaptation as in eq 10 is still needed. On the other hand, determinations of D_{segm} as reported by Buchachenko and Wassermann[14] for poly(vinylpyrrolidone) possibly could describe the termination rate constant as a function of conversion by segmental diffusion alone before and after the onset of entanglement and perhaps up to conversion close to the glass point. Thus, determinations of segmental diffusion coefficients in diluted and concentrated polymer solutions are very desirable.

For the evaluation of k_p and k_t, the efficiency must be known as a function of conversion. From our experiments a linear decrease of the efficiency with conversion resulted and could be described by the self-diffusion of the free radicals. A straight line connecting $f = f_0$ at $x = 0$ with $f = 0$ at x of the glass point seems to be a reasonable approximation.

Acknowledgment. We are obliged to the Arbeitsgemeinschaft Industrieller Forschungsvereinigungen, the Deutsche Forschungsgemeinschaft via the Sonderforschungsbereich für Chemie and Physik der Makromoleküle Mainz–Darmstadt, and the Fonds der Chemischen Industrie for support of this work.

Registry No. PMMA, 9011-14-7; methyl methacrylate, 80-62-6.

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