Polymerization of Methyl Methacrylate with Tris(π-allyl)chromium—Pyridine System

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ABSTRACT: The tris(π-allyl)chromium—pyridine system was found to be a good catalyst for the polymerization of MMA with quantitative yield. The kinetics and the mechanism of the polymerization were studied dilatometrically and gravimetrically at 0°C. Analysis of the data on the molecular weight of PMMA and of kinetic data showed that the initiation reaction was relatively fast and the termination reaction was negligible. The propagation rate constant was about $1.7 M^{-1} sec^{-1}$. The copolymerization of MMA with styrene (1 : 1) resulted in homopolymerization of MMA. This indicates that the mechanism is of an anionic type. The activating effect of pyridine taken in great excess with respect to the chromium compound (800 : 1) excludes the possibility of the coordinate-anionic mechanism of the polymerization of MMA.

KEY WORDS   Polymerization / Methyl Methacrylate / Tris(π-allyl)-chromium / Pyridine Activating Effect / Kinetics / Anionic Mechanism /

Tris(π-allyl)chromium (CrA₃) is a poor initiator for the polymerization of MMA which proceeds by a mechanism of the nonradical type.[1-3] The polymer yield in this process does not exceed 10% and the molecular weight of PMMA is of the order of 20000. In our study of the activation of CrA₃ by different Lewis bases we found that the systems CrA₃—pyridine and CrA₃—2, 2′-bipyridyl can be used as active initiators of the polymerization of MMA. They permit the preparation of PMMA of high molecular weight in quantitative yield. In order to elucidate the changes in the polymerization process caused by the activation, we studied the kinetics of the polymerization of MMA initiated by CrA₃—pyridine. Our results are compared with the data of Ballard and coworkers[2,3] on the polymerization of MMA with CrA₃ in the absence of complexing agents.

EXPERIMENTAL

Toluene was treated with concentrated sulfuric acid and sodium hydroxide and then refluxed with sodium in the presence of benzophenone (~1%) until it turned blue. Then it was distilled and stored over metallic sodium in argon.

Pyridine was purified by complexation with $HClO_4$[4] and by rectification on a column.

Methyl methacrylate was distilled on a column and stored over calcium hydride under an atmosphere of argon. Before use it was treated with activated alumina to remove all traces of inhibitor.

Tris(π-allyl)chromium was prepared by the reaction of $CrCl_3$ with allylmagnesium chloride at $-30°C$ in diethyl ether.[1] The quantity of CrA₃ required for the preparation of the catalyst was distilled at 10°C (0.01 mmHg) into an ampoule (Figure 1, I). Afterwards, pyridine pretreated with another portion of CrA₃ was distilled into the ampoule. The sealed-off ampoule was stored for 10 days at 20°C and subsequently sealed to a simple distribution device. The catalyst solution was dispensed volumetrically *in vacuo* into calibrated break-seal phials which were sealed off and stored in dry ice before use. An aliquot of the catalyst solution was used to determine the chromium concentration; after hydrolysis, the chromium was oxidized to bichromate with $K_2S_2O_8$ and titrated with ferrous sulfate.

The polymerization was carried out in a sealed
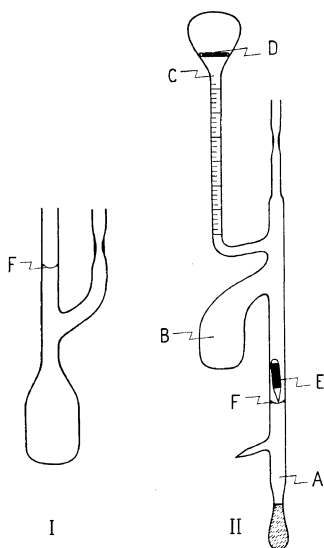
Figure 1. Ampoules for preparation of the catalyst (I) and for kinetic study of the polymerization (II): A, catalyst phial; B, bulb for monomer solution; C, dilatometer; D, magnetic stirrer; E, breaker; F, break-seal.

glass ampoule (Figure 1, II). The phial with the catalyst was attached to it shortly before the experiment and then the ampoule was linked to a vacuum line. The ampoule was heated at 200°C for 2 hr under vacuum (0.001 mmHg) with the exception of the catalyst phial. The solvent and the monomer were transferred by cold distillation and measured volumetrically at 20°C. The monomer solution was prepolymerized with a small quantity of CrA_3 and then distilled into the ampoule. The sealed ampoule was placed in a thermostat, the break-seal was crushed with the help of a magnet, and the reagent solutions were mixed by upturning the ampoule three times. The dilatometer was filled, the magnetic stirrer was switched on, and 3 min after the start of polymerization the conversion was followed dilatometrically. The polymerization was stopped by opening the ampoule and introducing acidified chloroform. The polymer was freed of the solvent and the unreacted monomer by evaporating them at room temperature in a stream of argon. Chromium compounds were removed by repeated heating of the polymer solution in ethyl acetate

with aqueous solution of hydrogen peroxide.

The molecular weights of the polymers were determined viscometrically in benzene solution by using the equation $[\eta]=8.69\times10^{-5}\times\bar{M}_n^{0.76}$.[5] Proper values of $\bar{M}_n$ are obtained if $\bar{M}_w/\bar{M}_n$ is 2 (Flory distribution). Gel-permeation chromatography of several polymer samples showed that in our case $\bar{M}_w/\bar{M}_n$ is approximately 3; hence the values calculated by using the above equation were divided by 3/2.

The NMR spectra were recorded on a JEOL C-60 HL spectrometer (an operating frequency of 60 MHz, o-dichlorobenzene, 190°C). Thermogravimetric measurements were made with a MOM derivatograph (Hungary, 1970).*

RESULTS AND DISCUSSION

It was found by preliminary experiments that the activity of the CrA_3—pyridine system was dependent on the time of ageing. A fresh solution of CrA_3 in pyridine exhibits almost the same activity as CrA_3 without pyridine. But after a day of aging the increase in activity of the catalytic system was very great; this made it possible to polymerize MMA in a 100-% yield. The highest activity of the system was attained by the aging of CrA_3 in pyridine at 20°C for 10—12 days. Prolonged aging (for a month) at room temperature led to deactivation.

The copolymerization of the equimolecular mixture of MMA and styrene initiated by the CrA_3—pyridine system resulted in the formation of the MMA homopolymer (99% of the MMA units), indicating that the polymerization proceeds by an anionic mechanism. The most suitable experimental conditions for kinetic studies were as follows: the temperature was 0°C, the solvent was toluene, the concentrations were MMA about 1 M, pyridine about 1 M, chromium about 10^{-3} M. The shape of the time—conversion curves depends on the temperature. At 25°C the high initial rate drops rapidly. At −15°C the initial rate is low and the kinetic curves have distinct induction periods. Figure 2 shows the kinetic curves of polymerization at 0°C. Table I shows the yields and molecular weights

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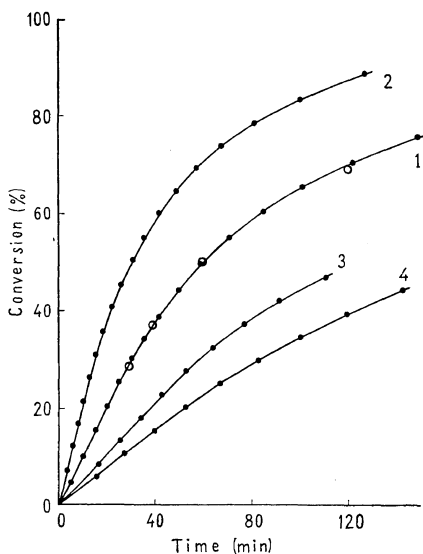
Figure 2. Kinetic curves of polymerization at 0°C: 1, $[M]_0$, $1 M$, $[I]_0$, $1.5 \times 10^{-3} M$; 2, $[M]_0$, $2 M$, $[I]_0$, $1.5 \times 10^{-3} M$, 3, $[M]_0$, $1 M$, $[I]_0$, $0.75 \times 10^{-3} M$; 4, $[M]_0$, $1 M$; $[I]_0$, $0.75 \times 10^{-3} M$; toluene; Py/CrA_3, 800 (1) (2) (3), 400 (4); blank circles denote gravimetric polymer yields.

**Table I.** Polymerization of MMA by CrA_3— pyridine system in toluene at 0°C

No.	$[MMA]_0$ M	$[Cr]$, $10^{-3} M$	$[Py]^a$, M	Reaction time, hr	Conversion, %	Mol. weight $\times 10^{-3}$
1	1	1.5	1.2	1.0	50	91
2	2	1.5	1.2	0.5	50	167
3	1	0.75	1.2	2.0	50	177
4	1	0.75	0.6	2.8	50	137
5	1	1.5	1.2	0.5	30	71
6	1	1.5	1.2	0.67	39	80
7	1	1.5	1.2	2.0	70	105
8	1	1.5	1.2	4.0	84	113
9	1	1.5	1.2	24	100	116
10	2	1.5	1.2	24	100	260

^{a} Py, pyridine.

of polymers obtained under the same conditions. The microtacticities of polymer samples obtained at $+25°$, $0°$, and $-15°C$ are the same according to the NMR data (in triads): $S=55\%$, $H=40\%$, $I=5\%$. Thermodegradation of these polymers begins to proceed near 240°C; this is general for PMMA prepared with anionic initiators.

The determination of the time (t) required to attain the same conversions (X) in experiments with various initial concentrations of reagents (Figure 2, curves 1—3) showed that the polymerization was first order with respect to initiator (I) and second order with respect to monomer (M). Furthermore, the polymerization rate depends on the pyridine concentration. A decrease in the pyridine concentration leads to a decrease in the polymerization rate (Figure 2, curves and 4) and also to a decrease in the molecular weight of polymer. Therefore we used the same pyridine concentration $1.2 M$ in all kinetic experiments. When another kinetic treatment was used, *viz.* plots of $\log[M]$ *vs.* t and $1/[M]$ *vs.* t, the order with respect to monomer was between 1 and 2. These data show the complexity of the mechanism, which evidently cannot be characterized by a simple kinetic equation. Therefore special attention was paid to the analysis of the time—conversion curves, especially because they showed good reproducibility over the entire conversion range.

Graphic differentiation of curve 1 (Figure 2) made it possible to estimate the values of the reduced rate $V/[M]$; the relationship of $V/[M]$ *vs.* t is shown in Figure 3. Since the polymerization rate can be expressed as $V=k_2[N^*][M]$, where k_2 is the propagation rate constant and $[N^*]$ is the concentration of active centers, the reduced rate may be regarded as a measure of $[N^*]$ at a given time.
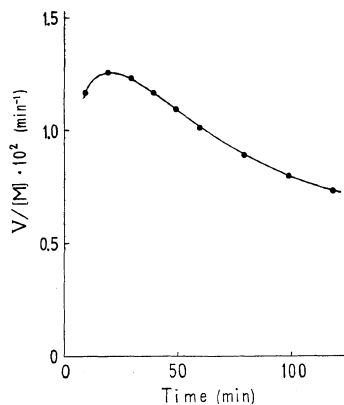
Figure 3. Reduced rate of polymerization *vs.* time: Polymerization conditions are the same as those in Figure 2, curve 1.
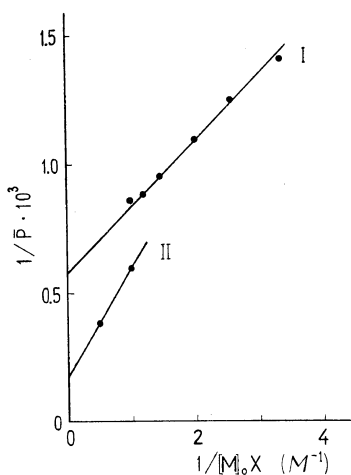
Figure 4. Reciprocal degree of polymerization *vs.* $1/[M]_0X$: I, $[M]_0$, $1\,M$; II, $[M]_0$, $2\,M$.

$$\frac{V}{[M]} = k_2[N^*] \qquad (1)$$

As shown in Figure 3 the plot of $[N^*]$ *vs.* t exhibits a maximum corresponding to about 20-% conversion. We used the data on the molecular weight of PMMA in order to explain the shape of the $V/[M]$—t curve. The experimental linear plot of $1/\bar{p}$ *vs.* $1/X$ ($\bar{p}$ is the average degree of polymerization) in the range of conversion from 30 to 100% (Figure 4, line I) was interpreted on the basis of the theoretical equation

$$\frac{1}{\bar{p}} = \frac{\int_0^t V_1\,dt}{\int_0^t V_2\,dt} + \frac{\int_0^t V_4\,dt}{\int_0^t V_2\,dt} \qquad (2)$$

where V_1, V_2, and V_4 are the rates of the initiation, propagation and transfer reaction, respectively. The slope of the line denotes the concentration of the polymer chains formed by initiation $[N] = \int_0^t V_1\,dt$. The constancy of $[N]$ in the conversion range investigated indicates that the initiation reaction is completed when conversion attains 30%. The intercept (Figure 4) corresponds to the second term of eq 2 and indicates that some transfer reaction takes place. The molecular weight of PMMA at $X=0.5$ in experiments with various $[I]_0$ (Table I, experiments 1 and 3) decreases greatly with increasing $[I]_0$; this can be explained by chain transfer to

the catalyst or to some species formed from it.

Thus it may be concluded that the ascending part of the $V/[M]$—t curve characterizes the initiation process which comes to an end in the region of the maximum. It seems probable that the descending part of the curve represents the reaction of deactivation of active centers, *i.e.*, kinetic termination. However, this assumption does not agree with the results of the quantitative treatment of the experimental data. The decrease in $[N^*]$ in the part of the curve corresponding to the time interval from 40 to 120 min (Figure 3) did not obey any simple kinetic order with respect to $[N^*]$. Satisfactory agreement with experimental data was achieved when it was assumed that the monomer takes part in the termination reaction ($V_3 = k_3[N^*][M]$). However, this assumption seems to be invalid in view of the proportionality between the molecular weights of PMMA and the monomer concentration (Table I, experiments 1 and 2, 9 and 10).

On the other hand, if the termination does not take place, it is possible that $[N^*]$ is influenced by the monomer concentration. As shown in Figure 5, the experimental points fit the relationship

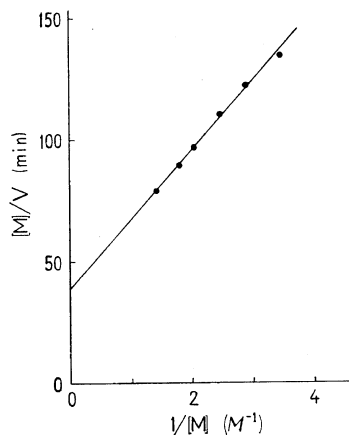$$\frac{V}{[M]} = \frac{A[M]}{B[M]+1} \qquad (3)$$

Figure 5. Reciprocal reduced rate of polymerization *vs.* reciprocal concentration of monomer: Polymerization conditions are the same as those in Figure 2, curve 1.
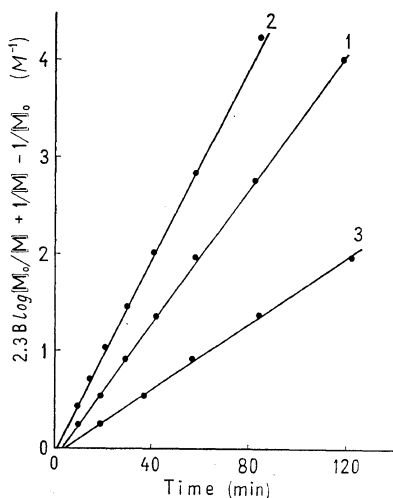
Figure 6. Plots of $2.3\,B \log [M]_0/[M] + 1/[M] - 1/[M]_0$ vs. time on the basis of eq 4: Polymerization conditions are the same as those in Figure 2 according to curve numeration.

where $A=3.5\times10^{-2}\,M^{-1}\,min^{-1}$ and $B=1.4\,M^{-1}$.

In order to check this relationship for experiments with various $[M]_0$ and $[I]_0$ (Figure 2, curves 1—3), we used the integral form of eq 3.

$$2.3B \log \frac{[M]_0}{[M]} + \frac{1}{[M]} - \frac{1}{[M]_0} = At \qquad (4)$$

The plots of the left-hand part of eq 4 vs. t (with $B=1.4\,M^{-1}$) show that the experimental points fall satisfactorily on straight lines (Figure 6) which do not pass through the origin. This is evidently caused by the existence of a period for the formation of N. It should be noted that the value of A depends on $[M]_0$ and $[I]_0$.

In order to explain eq 3 we accepted the concept according to which there are two forms of growing chains which differ markedly in their activities. This hypothesis has been repeatedly proposed by the authors who have examined anionic polymerization of PMMA.[6,7] We believe that the total number of growing chains [N] remains constant at $X\geq30\%$ and is equal to the sum of the concentrations of the active form $[N^*]$ and of the temporarily deactivated (dormant) form $[N_d]$.

$$[N]=[N^*]+[N_d] \qquad (5)$$

Both forms are capable of mutual transforma-

tions in the course of the polymerization process. The deactivation proceeds spontaneously at the rate

$$V_d=k_d[N^*] \qquad (6)$$

while the inverse transformation (reinitiation) takes place with the participation of the monomer

$$V_a=k_a[N_d][M] \qquad (7)$$

A steady state is attained when $V_d=V_a$; also using eq 5—7 the result is

$$[N^*]=\frac{\dfrac{k_a}{k_d}[N][M]}{\dfrac{k_a}{k_d}[M]+1} \qquad (8)$$

The substitution of eq 8 into eq 1 gives

$$V=\frac{k_2\dfrac{k_a}{k_d}[N][M]^2}{\dfrac{k_a}{k_d}[M]+1} \qquad (9)$$

Equation 9 is identical with the experimental eq 3 where

$$A=k_2\frac{k_a}{k_d}[N] \qquad (10)$$

and

$$B=\frac{k_a}{k_d} \qquad (11)$$

The above mentioned dependence of parameter A on $[I]_0$ and $[M]_0$ can be attributed to their influence on the total number of growing chains [N]. It has been stated that the effectiveness of the initiation of various polar vinyl monomers including MMA depends on the monomer concentration.[7] Since the initiation is completed at $X\leq30\%$, the following expression for [N] is possible

$$[N]=f([M]_0)[I]_0 \qquad (12)$$

where $f([M]_0)$ is the factor of the efficiency of initiation.

The molecular weight data (slopes of lines I and II in Figure 4) also confirm the dependence of [N] on $[M]_0$. It is noteworthy that the ratio $[N]_{II}/[N]_I=1.6$ (Figure 4) virtually coincides with the ratio $A_2/A_1=1.5$ (Figure 6).

It follows from eq 10 and 11 that

$$k_2 = \frac{A}{B[\text{N}]} \qquad (13)$$

The value of k_2 calculated according to eq 13 is $1.0 \times 10^2 \, M^{-1} \, \text{min}^{-1}$ or $1.7 \, M^{-1} \, \text{sec}^{-1}$.

If we write the kinetic equation in its detailed form

$$V = \frac{k_2(k_\text{a}/k_\text{d})f([\text{M}]_0)[\text{I}]_0[\text{M}]^2}{(k_\text{a}/k_\text{d})[\text{M}]+1} \qquad (14)$$

we can explain the reason why the kinetic order with respect to monomer depends on the method of its determination. If the time required to attain the same conversions is used for calculation, one should bear in mind the difference in $f([\text{M}]_0)$. On the other hand, if the order is determined according to the changes in monomer concentration in the course of polymerization, them $f([\text{M}]_0)$ remains constant for each time—conversion curve. In the former case the apparent kinetic order should be higher.

When we compare our data on the polymerization of MMA initiated by CrA₃—pyridine with the data of Ballard and coworkers[1-3] concerning the unactivated CrA₃, we note first of all that in both cases anionic polymerization takes place. This conclusion is drawn from the fact that the product of copolymerization of MMA with styrene (1 : 1) is an almost pure PMMA (99% of MMA units in our case). The activation of CrA₃ by pyridine causes remarkable changes in the values of the rate constants of individual reactions of the polymerization process. The initiation rate increases while the termination reaction becomes negligible.

It is noteworthy that the pyridine which activates CrA₃ in the polymerization of MMA acts as an inhibitor in the polymerization of ethylene initiated by organometallic compounds of transition metals.[8] The polymerization of MMA evidently proceeds without preliminary coordination of the monomer on an active center and does not belong to the coordinate-anionic type.

REFERENCES

1. D. G. H. Ballard, W. H. Janes, and T. Medinger, *J. Chem. Soc, Sect. B*, 1168 (1968).
2. D. G. H. Ballard and T. Medinger, *ibid.*, 1177 (1968).
3. D. G. H. Ballard and J. V. Dawkins, *Makromol. Chem.*, **148**, 195 (1971).
4. "Methoden der organischen Chemie," Vol. II, Houben-Weyl, 1953, p 324.
5. T. G Fox, J. B. Kinsinger, H. F. Mason, and E. M. Schuele, *Polymer*, **3**, 71 (1962).
6. M. Szwarc, "Carbanions, Living Polymers and Electron Transfer Processes", Interscience, New York, N.Y., 1968.
7. B. L. Erussalimsky, "Ionic Polymerization of Polar Monomers" (in Russian), Nauka, Leningrad, 1970.
8. D. G. H. Ballard, *Advan. Catal.*, **23**, 263 (1973).