Magnesium—Benzophenone Ketyl as an Initiator of Anionic Polymerization of Methyl Methacrylate

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ABSTRACT: Polymerization of methyl methacrylate was studied in tetrahydrofuran with magnesium—benzophenone ketyl as initiator. According to the results of optical absorption studies on the reaction of the initiator as well as of conventional polymerization experiments; it is concluded that (1) the polymerization proceeds *via* the anionic mechanism, (2) the initiation reaction between the ketyl anion and the monomer shows an activation energy of 4 kcal/mol and a rate constant of $1.6 \times 10^{-2} M^{-1}\mathrm{sec}^{-1}$ at $-25°C$, and (3) the chain-transfer reaction occurs slowly through electron transfer to benzophenone in the reaction system with an activation energy of 2 kcal/mol and a rate constant of $1.3 \times 10^{-1} M^{-1}\mathrm{sec}^{-1}$ at $-25°C$. The results also suggested that the initiation efficiency is not much lower than unity and that the propagation rate constant is as low as $10^{-1} M^{-1}\mathrm{sec}^{-1}$ at $-20°C$.

KEY WORDS   Anionic Polymerization / Methyl Methacrylate / Benzophenone Ketyl / Radical Anion / Absorption Spectrum / Initiation Mechanism / Chain Transfer / Electron Transfer /

The present investigation is aimed at understanding the initiation reaction in anionic polymerization of methyl methacrylate (MMA) in tetrahydrofuran (THF) using magnesium—benzophenone ketyl as initiator. In contrast to the sodium—benzophenone ketyl studied previously in its role in initiating the anionic polymerization,[1] magnesium—benzophenone ketyl forms a dimeric structure with a dipositive cation.

Since the first studies by Inoue, *et al.*[2] and Smith, *et al.*[3] ketyl anions are known to initiate anionic polymerization of vinyl monomers such as MMA and acrylonitrile.[1,4,5] However, the mechanism involved has not yet been elucidated for a polymerization initiated by ketyl anions generated by reducing with alkaline—earth metals. The only study so far is that reported by Tsuruta, *et al.*,[6] who presumed that the polymerization of MMA by magnesium—benzophenone ketyl was anionic in nature and found that the stereo-specificity of polymer obtained was inferior to that obtained in the ordinary anionic polymerization initiated by organometallic catalysts.

Although the nature of ketyl anions is rather complex because of variety of their forms, their behavior in solutions has been studied extensively within the last decade.[7] It is now well understood that at least four entities (free ketyl anion, ion-pair, paramagnetic ketyl dimer and diamagnetic dimer of pinacolate form) are equilibrated with each other in solution. These entities are different from each other not only in their structure but also in their reactivity. In view of the recent advance in the study of the ionic equilibria in a solution of benzophenone ketyl, the present authors investigated the mechanism involved in the anionic polymerization of MMA in THF in purified reaction system under well specified conditions with monomeric sodium—benzophenone ketyl as an initiator.[1] The study is extended here to magnesium—benzophenone ketyl as another initiator, which was shown by electron spin resonance (ESR) studies to form the dimeric ketyl (two anions are associated with a single dipositive metal ion) in THF solution.[8] Attention is especially focussed in the present investigation on the spectroscopic studies on the reaction between the initiator and the monomer in reference to the analysis of polymer obtained.

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EXPERIMENTAL

Chemicals

MMA, THF and benzophenone were purified as described previously.[1] Mercury of reagent grade (Wako Pure Chemicals Ind. Co., Ltd.) was used as received without further purification. Magnesium ribbon (Cameleon analytical grade, Kishida Chemicals Co., Ltd.) was polished with sand-paper and cut in pieces immediately before use.

Preparation of Magnesium—Benzophenone Ketyl

The solution of magnesium—benzophenone ketyl was prepared in a glass apparatus similar to that shown in Figure 1 in the previous paper.[1] In the present study however, the ampoule containing the sodium mirror was replaced with a side-arm through which mercury and magnesium are put into the vessel A. The whole apparatus was connected to a vacuum line, evacuated and flamed thoroughly. The side-arm was then opened for several pieces of magnesium and mercury to be introduced into the vessel A. The apparatus was evacuated after sealing the end of the sid-arm and kept overnight. Magnesium amalgam was thus obtained in the vessel A in vacuo. A known amount of THF was vacuum-distilled on to the amalgam and degassed by freezing—pumping—thawing cycles under a vacuum line by sealing at the constriction. Benzophenone was dissolved in THF through a break seal and made contact with the amalgam to form the ketyl anion. After the desired concentration of the ketyl was attained (the concentration was estimated from its blue color), the solution was filtered to remove the amalgam and divided into small aliquots. The reaction of benzophenone with magnesium amalgam was much slower than that between benzophenone and sodium, so that a concentration of benzophenone as high as 10^{-2} M was needed to prepare 10^{-4} M of the ketyl anion within an hour.

Measurements

The reaction between the initiator and the monomer was examined by observing the change in the optical absorption due to the ketyl anion after mixing the monomer into the solution.

Polymerization was carried out by mixing the monomer into the solution of magnesium—benzophenone ketyl in vacuo through a break seal as described previously.[1] The product polymer was precipitated in methanol. Either a GPC or a viscometric method was used in determining the molecular weight of the polymer and its distribution. Toluene was used as solvent in the viscometry, where the molecular weight was evaluated from the relation, $[\eta] = 6.8 \times 10^{-5} M_v^{0.71}$.[9]

Determination of Extinction Coefficient of Magnesium—Benzophenone Ketyl

The extinction coefficient of magnesium—benzophenone ketyl was determined with reference to that of sodium—benzophenone ketyl both in THF. The concentration of both the ketyls was determined relative to each other from the double integration of the derivative ESR spectra of the ketyls in the same solutions as were subjected to the optical measurements. The absolute concentration of sodium—benzophenone ketyl was obtained on the basis of its reported extinction coefficient $(12,000\ M^{-1}\mathrm{cm}^{-1})$,[7] and then the extinction coefficient of magnesium—benzophenone ketyl was obtained from the observed optical density. It should be noted that the concentration of the magnesium—benzophenone ketyl is just one half the concentration of the ketyl anion determined by ESR, because the alkaline—earth metal ketyl is known to be in the dimeric form (two ketyl anions are associated with a dipositive ion).
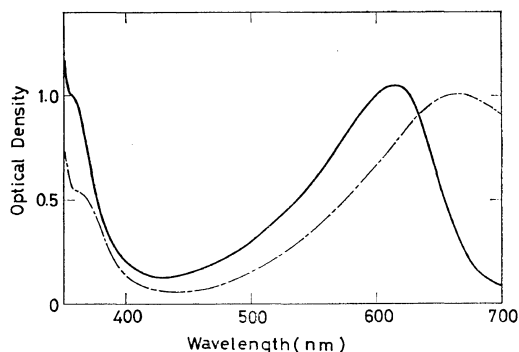

Figure 1. Optical absorption spectra of magnesium—benzophenone ketyl (solid line) and sodium—benzophenone ketyl (dashed line) in tetrahydrofuran at room temperature.

RESULTS

Absorption Spectra of Magnesium—Benzophenone Ketyl

Figure 1 shows the optical absorption spectrum of magnesium—benzophenone ketyl in THF together with that of sodium—benzophenone ketyl for comparison. The former spectrum shows a broad maximum at about 610 nm, while the latter has a maximum at 670 nm. By determining the concentration of the former ketyl in the THF solution relative to that of the latter, it was found that the solution of 1.2×10^{20} spins/l of magnesium—benzophenone ketyl gave an optical density of 0.888 at 610 nm for a 0.5 cm optical path. Thus, the extinction coefficient of the magnesium—benzophenone ketyl was determined to be 18,000 $M^{-1}cm^{-1}$. Throughout the present investigation, the concentration of the initiator was determined by doubling the concentration of the magnesium ketyl obtained on the basis of this extinction coefficient.

Figure 2 shows the Beer—Lambert plot for the ketyl at the absorption maximum at 610 nm. In order to minimize the effect of trace of oxygen and moisture during this measurement, the concentration was varied by vacuum-distilling a fraction of solvent within a closed glassware. The linear relationship indicates that the extinction coefficient is unchanged over the whole concentration range examined $(10^{-5}$—$10^{-4}\ M)$, that only the dimeric ketyl is present in the solution, and that the dissociation into monomeric form or the formation of aggligomer does not need to be taken into account. This observation
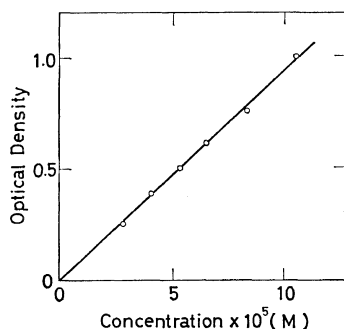
is in agreement with the results obtained by ESR measurements.[8]

Reaction between the Initiator and the Monomer

On adding MMA into the THF solution of magnesium—benzophenone ketyl, the blue color characteristic to the ketyl anion disappears rapidly. Figure 3 shows the change in the optical density at 610 nm after the addition of the monomer, representatively at 0°C. Evidently the ketyl anion decreases in its concentration, but a fraction remains for a long time. Neither a first-order kinetic nor a second-order one fits the observed decay curve as a whole. It is, however, well analyzed as a superposition of an exponentially decaying part (see the insert of Figure 3) and a long-remaining part, though the exponential plots deviate from the straight line at a very early period because of the time required for the temperature of the reaction system to become stable.
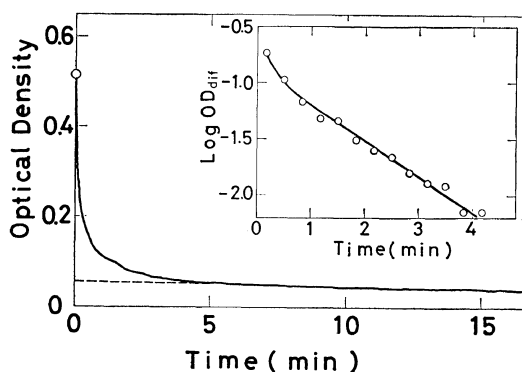

Figure 3. The decay of the optical density of magnesium—benzophenone ketyl monitored at 610 nm after mixing with MMA. The insert represents the first-order plot of the initial fast decaying portion: Initiator, $1.15 \times 10^{-4}\ M$; MMA, 0.42 M; benzophenone, $8.3 \times 10^{-3}\ M$; temperature, 0°C.

It should be noted that the exponential decay becomes faster and the fractional ratio of the long-remaining part decreases with increasing temperature. The exponential decay is interpreted as due to the reaction between the ketyl anion and the monomer as in the case of the anionic polymerization of MMA initiated by sodium—benzophenone ketyl.[1]

Figure 2. Dependence of the optical density at 610 nm upon the concentration of magnesium—benzophenone ketyl in tetrahydrofuran at 20°C.

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Polymerization

Poly-MMA is also obtained by adding the monomer into the solution of the ketyl anion. Figure 4 shows a time—conversion curve at −20°C. The polymerization proceeds for a rather long time compared to the decay of the ketyl anion, and then reaches a limiting value. The effect of temperature is qualitatively illustrated in Figure 5, where the conversion at a fixed time is plotted as a function of temperature. Obviously there is a maximum at about −20°C, above which the polymer yield decreases with increasing temperature.

Figure 6 shows a relationship between the molecular weight of polymer determined by the viscometric method and the polymerization time. The molecular weight tends to a plateau value at a later period of polymerization. The mo-

lecular weight distribution of the polymer was examined by the GPC method. The results are summarized in Table I. The distribution is much
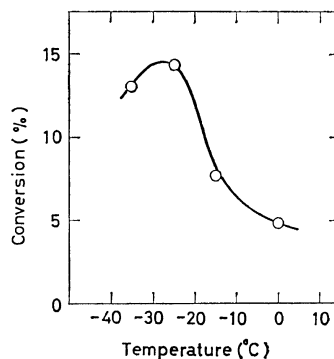
Figure 5. Temperature dependence of the polymer yield at a fixed polymerization time of 2 hr after mixing MMA (3.71 M) with the initiator (6.6 × $10^{-4} M$).
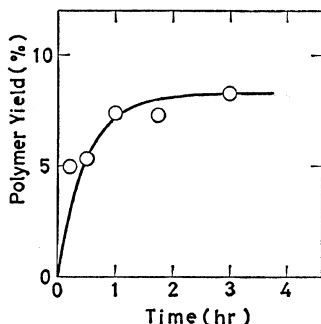
Figure 4. The dependence of polymer yield upon time after mixing MMA with magnesium—benzophenone ketyl, observed at −20°C for $2.2 \times 10^{-4} M$ of the initiator, 3.7 M of MMA and $1.0 \times 10^{-2} M$ of benzophenone. The solid line shows the curve simulated from eq 6 for $k_p = 2.17 \times 10^{-1} M^{-1}\mathrm{sec}^{-1}$ and $k_t = 5.50 \times 10^{-4} \mathrm{sec}^{-1}$.
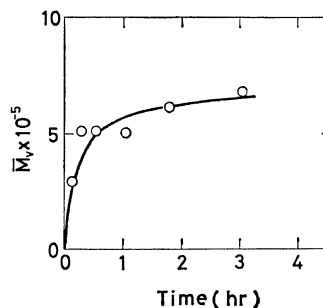
Figure 6. The viscosity-averaged molecular weight of polymer obtained in the polymerization of MMA initiated by magnesium—benzophenone ketyl as a function of the polymerization time at −20°C: Initiator, $2.2 \times 10^{-4} M$; MMA 3.7 M; benzophenone, $1.0 \times 10^{-2} M$.

Table I. Analysis of polymer obtained in the anionic polymerization of MMA initiated by magnesium-benzophenone ketyl in THF

Temp, °C	Time, min	Initiator, $M \times 10^4$	Monomer, M	Polymer yield, %	$\bar{M}_n$, ×10^{-4}	$\bar{M}_w/\bar{M}_n$	Ratio[a]
−20	15	2.22	3.71	5.0	4.54	7.6	2.0
−20	180	2.12	3.71	8.3	5.38	3.8	2.7
−35	120	7.02	3.71	12.0	8.78	4.7	0.75
0	60	3.86	3.80	3.4	2.75	3.6	1.2

[a] Ratio of the number of polymer chains obtained to the number of initiator. The number of initiator is twice that of magnesium—benzophenone ketyl determined on the basis of the extinction coefficient of 18,000 $M^{-1}\mathrm{cm}^{-1}$.

broader in this case than in the polymerization by sodium—benzophenone ketyl as initiator ($\bar{M}_w/\bar{M}_n$ was typically 2).[1] It should be noted that the value as high as 2.7 is obtained for the ratio of the number of polymer chains to the number of the initiator fed.

Copolymerization

In order to confirm the nature of the polymerization, the copolymerization was also carried out with acrylonitrile. The copolymerization curve (see Figure 7) agrees well with that for the same combination of monomers initiated by phenyl magnesium bromide.[10] This indicates that the present polymerization proceeds via an anionic mechanism.
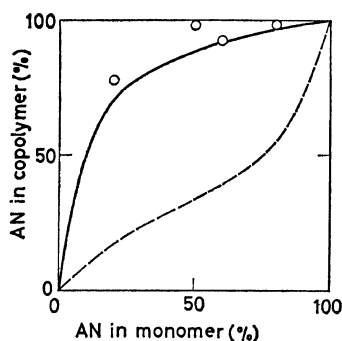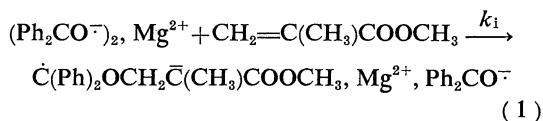

Figure 7. Relation between the monomer composition and polymer composition in copolymerization of methyl methacrylate with acrylonitrile initiated by magnesium—benzophenone ketyl in tetrahydrofuran at 0°C. The solid and dashed lines show the reported curves for the anionic and radical polymerizations, respectively.[10]
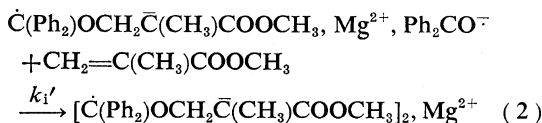
DISCUSSION

Reaction between the Initiator and MMA

The simultaneity of polymer formation with the decay of benzophenone ketyl anion together with the copolymerization with acrylonitrile indicates that the polymerization of MMA initiated by magnesium—benzophenone ketyl proceeds in the anionic mechanism. The initiation reaction is, from the analogy with the polymerization initiated by sodium—benzophenone ketyl,[1] thought to be the addition of the initiator to the monomer,

$$(Ph_2CO^-)_2,\ Mg^{2+}+CH_2=C(CH_3)COOCH_3 \xrightarrow{k_i}$$

$$\dot{C}(Ph)_2OCH_2\bar{C}(CH_3)COOCH_3,\ Mg^{2+},\ Ph_2CO^- \quad (1)$$

which may be followed by the initiation of another propagating chain.

$$\dot{C}(Ph_2)OCH_2\bar{C}(CH_3)COOCH_3,\ Mg^{2+},\ Ph_2CO^-$$

$$+CH_2=C(CH_3)COOCH_3$$

$$\xrightarrow{k_i'} [\dot{C}(Ph_2)OCH_2\bar{C}(CH_3)COOCH_3]_2,\ Mg^{2+} \quad (2)$$

The rate constants, k_i and k_i', are possibly different from each other, but they are not distinguishable experimentally. Therefore, we assume arbitrarily that $k_i=k_i'$ throughout the analysis of data.

A significant feature of the decay of the ketyl anion upon mixing with the monomer is that a fraction of its initial concentration remains for a long time. Such a feature was observed for the reaction between sodium—benzophenone ketyl and MMA in the presence of excess benzophenone added intentionally.[1] In the present reaction system, a considerable amount of benzophenone coming from the preparation procedure of the ketyl anion is present and thought, as in the previous case, to accept an electron from a propagating carbanion,

$$\sim C^-,\ Mg^{2+},\ {}^-C\sim +Ph_2CO$$

$$\xrightarrow{k_{tr}} \sim C^-,\ Mg^{2+},\ Ph_2CO^- + \cdot C\sim \quad (3)$$
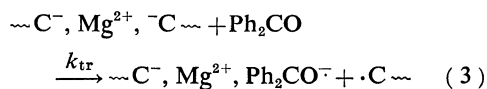
to regenerate the initiator, which in turn initiates additional polymer chains. Based on the above reaction scheme, the following equation is readily derived for the decay of the ketyl anion,[1]

$$\frac{[Ph_2CO^-]}{[Ph_2CO^-]_0} = \frac{k_i[MMA]}{k_i[MMA]+k_{tr}[Ph_2CO]}$$

$$\times \exp\{-(k_i[MMA]+k_{tr}[Ph_2CO])t\}$$

$$+ \frac{k_{tr}[Ph_2CO]}{k_i[MMA]+k_{tr}[Ph_2CO]} \quad (4)$$

under the assumption that the initiation efficiency is unity and the termination reaction is ignored. In the above equation, the left-hand side denotes the normalized concentration of the ketyl anion, and $[Ph_2CO]$ represents the concentration of benzophenone present in the reaction system. The long-remaining fraction of the ketyl anion corresponds to the second term in the right-hand side of the equation and results from the equilibrium between the consumption of the initiator through the reactions (1) and (2) and its regeneration through the reaction (3).
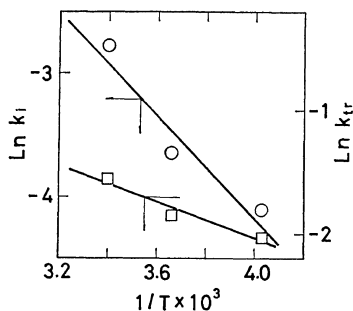
Figure 8. Arrhenius plots of the initiation rate constant, k_i, and the chain-transfer rate constant, k_{tr}, obtained from the decay curves of the initiator.

According to eq 4, the rate constants, k_i and k_{tr}, can be evaluated from the initial exponential decay, the amount of the long-remaining fraction and the concentration of benzophenone and MMA in the reaction system. Because the long-remaining fraction itself decays very slowly, its extrapolated value at zero time (see the dashed line in Figure 3) was equated to the second term of the right-hand side of eq 4 throughout the quantitative analysis of observed decay curves. Thus obtained k_i and k_{tr} are shown in Figure 8 as a function of temperature. Arrhenius plots are somewhat scattered, but give an estimate of activation energies, 4 and 2 kcal/mol, for k_i and k_{tr}, respectively. The former value is less than half the activation energy previously determined for the reaction between sodium—benzophenone ketyl and MMA.[1] The small activation energy for k_{tr} seems to be consistent with the presumed electron transfer reaction (3) which transforms the propagating carbanion into the relatively stable ketyl anion.

When the monomer concentration was increased, the long-remaining fraction was found to decrease by such amount as would be expected from the value of k_i and $k_{tr}[Ph_2CO]$, though the initial exponential decay becomes too fast to be recorded properly. This observation gives a good test for the validity of the eq 4.

The slow decay of the long-remaining fraction is attributable to a gradual decrease in the concentration of the propagating chain ends, though it is neglected in quantitative analysis of the decay curves. The decrease in the concentration of the chain ends is, in turn, attributable to the

termination reaction due to the attack of the propagating carbanion or the initiator (regenerated by the chain-transfer reaction) toward the carbonyl group.[11] If one expresses the rate of the termination reaction with a first-order rate constant, k_t, the neglect of the slow decay means that k_t should be small enough compared with any rate constants involved in eq 4. It turns out that $k_t \ll k_{tr}[Ph_2CO]$ and, therefore, $k_t \lesssim 10^{-4}\ \mathrm{sec}^{-1}$.

Kinetic Data of Polymerization

In order to substantiate the data obtained from the optical absorption measurements of the reaction between magnesium—benzophenone ketyl and MMA, conventional polymerization experiments were alo carried out by mixing the monomer into the THF solution of the ketyl anion mostly at $-20°C$, where the polymerization was found to proceed at its highest efficiency. It should be noted that the monomer concentration in the polymerization experiments was generally ten times as high as that in the optical absorption measurements in order that the polymer yield reached a measurable conversion within a reasonable polymerization time (a few hours).

Under the condition of the polymerization experiments, the initial exponential decay of the initiator is thought to almost complete within one minute because of the high monomer concentration. In contrast, the time—conversion curves continue to increase for over an hour and then tend to a limiting value depending on temperature (see Figure 4). This behavior suggests that the termination reaction occurs, though very slowly, in the present polymerization. The termination is expected to be a first-order reaction with respect of the concentration of propagating chain, which varies as

$$[P^-] = [P^-]_0 \exp(-k_t t), \qquad (5)$$

where $[P^-]_0$ denotes the concentration immediately after the completion of the rapid initiation reaction. Accordingly, the increase in the polymer yield should follow the equation,

$$-\frac{d[MMA]}{dt} = k_p[MMA][P^-]_0 \exp(-k_t t)$$

which is readily integrated, with the initial condition that $[MMA] = [MMA]_0$ at $t = 0$, as

$$\ln \frac{[\text{MMA}]_0}{[\text{MMA}]} = \frac{k_p}{k_t}[\text{P}^-]_0 \exp\left(-k_t t\right) \qquad (6)$$

According to the eq 6, the value of k_t is determined to be $5 \times 10^{-4}\,\text{sec}^{-1}$ at $-20°C$ from the observed time—conversion curve by the curve-fitting method.

If the termination reaction is brought about by the side reaction of the propagating carbanion to the carbonyl group of both monomer and polymer, the apparent rate constant k_t is expressed by a second-order rate constant as $k_t'[\text{MMA}]_0$. If the carbonyl group of the monomer only is responsible for the termination reaction, k_t should be replaced by $k_t'[\text{MMA}]$. Even in the latter case however, k_t can be approximated by $k_t'[\text{MMA}]_0$ in low consumption of the monomer. Thus, k_t in the optical absorption measurements (where the initial monomer concentration is one tenth of that in the polymerization experiments) is about $5 \times 10^{-5}\,\text{sec}^{-1}$, well below the required limit of $10^{-4}\,\text{sec}^{-1}$. Therefore, this polymerization datum validates the assumption used in the analysis of the decay curve that the termination reaction is slow enough to be ignored. The polymerization proceeds less efficiently with increasing temperature above $-20°C$ (see Figure 5). This may be interpreted by the termination reaction due to the carbonyl attack of the propagating carbanion which was reported to be pronounced at higher temperatures.[12]

If $[\text{P}^-]_0$ is replaced by the initial concentration of the initiator $[\text{Ph}_2\text{CO}^-]_0$, the ratio k_p/k_t and therefore the value of k_p can be estimated from the limiting conversion. Typically, the value of $0.2\,M^{-1}\,\text{sec}^{-1}$ was obtained for k_p at $-20°C$. This value, though reliable only in order of magnitude, seems to be surprisingly smaller than the value recently reported for the anionic polymerization of MMA in THF.[12,13] This difference may be attributable either to the presence of excess benzophenone in the reaction system or to the specific nature of the propagating chain ends two of which associate with a single counter-ion, Mg^{2+}, in the present polymerization. However, we are not going into this problem further, because no information is obtained from the optical absorption measurements on the propagation reaction.

The ratio of the number of polymer chains to

the number of initiator fed reaches as high as 2.7 at $-20°C$ (see Table I). This indicates that one initiator gives more than one polymer chain after a long polymerization time and that the chain transfer reaction is involved in the present polymerization. This view is consistent with the tendency that the molecular weight of polymer reaches a plateau value (see Figure 6) somewhat quicker than the time—conversion curve does.

On the basis of the chain transfer mechanism (3) presumed previously, the increase in the number of polymer chains should follow the relationship,

$$\frac{d[\text{P}]}{dt} = k_{tr}[\text{P}^-][\text{Ph}_2\text{CO}]$$

which is integrated with the initial condition of $[\text{P}^-]=[\text{P}^-]_0$, after substituting the eq 5, as

$$[\text{P}] = [\text{P}^-]_0\left[1 + \frac{k_{tr}}{k_t}[\text{Ph}_2\text{CO}]\{1 - \exp\left(-k_t t\right)\}\right]$$

This relationship gives a limiting value of $[\text{P}^-]_0\{1 + \{k_{tr}[\text{Ph}_2\text{CO}]/k_t\}\}$ at $t=\infty$. On the other hand, the limiting value of the monomer consumed is readily obtained from the eq 6 as $[\text{MMA}]_0\{1 - \exp\left(-k_p[\text{P}^-]_0/k_t\right)\}$. The limiting value of the degree of polymerization is therefore given by

$$\overline{\text{DP}} = \frac{[\text{MMA}]_0\{1 - \exp\left(-k_p[\text{P}^-]_0/k_t\right)\}}{[\text{P}^-]_0\{1 + k_{tr}[\text{Ph}_2\text{CO}]/k_t\}} \qquad (7)$$

It can be calculated from the value of $k_t=5 \times 10^{-4}\,\text{sec}^{-1}$ and $k_p=0.2\,M^{-1}\,\text{sec}^{-1}$ estimated from the polymerization data at $-20°C$ and that of $k_{tr}[\text{Ph}_2\text{CO}]=10^{-3}\,\text{sec}^{-1}$ estimated from the analysis of the decay curve at $-25°C$ (see Figure 8), if one used $[\text{Ph}_2\text{CO}^-]_0$ for $[\text{P}^-]_0$. Thus obtained $\overline{\text{DP}}$ is 480, which seems to be in agreement with the degree of polymerization at $-20°C$ for the long polymerization time actually determined by the GPC method (see Table I and note that the molecular weight of MMA is 100).

Although the recombination between the polymer radicals formed by the reactions (1), (2), and (3) and the radical polymerization due to them (probably very little, if any) were ignored in the above estimation of the degree of polymerization, this agreement gives an qualitative evidence that the proposed reactions (1), (2), and (3) are really involved in the anionic polymeri-

zation of MMA initiated by magnesium—benzophenone ketyl and validates the analysis of the decay of the ketyl anion in reacting with MMA. It also suggests that the initiation efficiency is close to unity (at least, not much lower than unity) because the initial concentration of propagating carbanions could be replaced by the concentration of the initiator fed, and that the k_p value is really as low as $10^{-1} M^{-1} \sec^{-1}$ in the present polymerization.

Conclusion

Dimeric benzophenone ketyl associated with Mg^{2+} effectively initiates the anionic polymerization of MMA in THF solution, as does monomeric sodium—benzophenone ketyl. The remarkable features in this polymerization are that the propagating chain has a long lifetime, during which the chain transfer reaction occurs through the electron transfer from the propagating carbanion to benzophenone present in the solution and the regeneration of the initiator. The rate constants, k_i and k_{tr}, are 0.016 and 0.13 $M^{-1} \sec^{-1}$ at $-25°C$, of which activation energies are 4 and 2 kcal/mol, respectively. Compared with the previous results for the polymerization initiated by sodium—benzophenone ketyl (k_i was 0.012 $M^{-1} \sec^{-1}$ at $-10°C$ with the activation energy of 13 kcal/mol), the activation energy is much smaller in the present polymerization.

The results also suggests the very low value of k_p, $10^{-1} M^{-1} \sec^{-1}$ at $-20°C$ under the assumption that the initiation efficiency is unity. Although this assumption was qualitatively substantiated in the present investigation, the quantitative evaluation of the initiation efficiency is experimentally difficult but highly desirable.

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