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Living Cationic Polymerization of Isobutylene with Mixtures of Titanium Tetrachloride/Titanium Tetrabromide

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ABSTRACT: The effect of ligand of Lewis acid on the cationic polymerization of isobutylene (IB) using $TiCl_4/TiBr_4$-mixed co-initiator is reported. The polymerization proceeds in a living fashion; however, the polymerization rate decreases with decreasing $TiCl_4/TiBr_4$ ratio. The active co-initiator in this polymerization system is the mixed dimer, $Ti_2Cl_xBr_{(8-x)}$, not the dimer of $TiCl_4$ or $TiBr_4$. From the molecular weight distribution vs conversion plots, the rate constant of deactivation, k_{-i}, and ionization, k_i^{app}, the apparent equilibrium constant of ionization, k_i^{app}, and the thermodynamic parameters are calculated and discussed. By the stepwise replacement of Cl to Br the Lewis acidity decreases, which results in a decreased ionization rate constant while the deactivation rate constant remains essentially unchanged. Therefore, the decreasing overall rates of polymerization with decreasing $TiCl_4/TiBr_4$ ratio are exclusively due to the lower equilibrium constant of ionization, which results in lower ion pair concentration.

Introduction

There are only a few Lewis acids that have been known to induce the living cationic polymerization of isobutylene (IB). Titanium tetrachloride ($TiCl_4$) is by far the most commonly used Lewis acid, also suitable for the living sequential block copolymerization of IB with styrene. Therefore, application of $TiCl_4$ in industrial-scale polymerization is also well advanced. The polymerization of IB in conjunction with $TiCl_4$ is well studied, and kinetic and mechanistic details have been established recently.[1] The active co-initiator is believed to be the dimer, Ti_2Cl_8. Because of the low equilibrium constant of $TiCl_4$ dimerization (K_{D0} is estimated at about 1 L mol^{-1} at −80 °C), the concentration of Ti_2Cl_8 is low. Therefore, a relatively high $[TiCl_4] \sim 0.02-0.06$ M is necessary to achieve reasonable polymerization rates, and the majority of $TiCl_4$ present as a monomeric weak Lewis acid is inactive as co-initiator.

Alkylaluminum chloride has been studied recently as another potential Lewis acid for the living polymerization of IB.[2,3] With $MeAlCl_2$ or $Me_{1.5}AlCl_{1.5}$ as co-initiators, the polymerization proceeds very rapidly in a living manner even at low co-initiator concentration (∼0.001 M).[2] On the other hand, using Me_2AlCl, the polymerization of IB is very slow even at $[Me_2AlCl] \sim 0.01$ M. Preliminary results suggest that $MeAlCl_2$ is more than 10^5 times stronger Lewis acid than Me_2AlCl. These facts indicate that a slight change in structure of Lewis acid may affect the Lewis acidity and polymerization behavior dramatically.

Recently, we have reported on the effects of solvent polarity, temperature, and the nature of Lewis acid on the rate constants of propagation, ionization (activation), and reversible termination (deactivation) in the carbocationic polymerization of IB.[4] The absolute propagation rate constant for ion pairs ($k_p^{\pm}$) is independent of the nature of Lewis acid; thus, the Lewis acidity affects only the concentration of active carbocationic center. To obtain an appropriate concentration of active species for living cationic polymerization, accurate modification of Lewis acidity is needed. Because of the lack of knowledge on tailoring Lewis acidity for living cationic polymerization, however, studies on small, stepwise variation of Lewis acidity and their effect on living cationic polymerization are desired.

In starting studies in this area, the effect of ligand of Lewis acid on the cationic polymerization of IB using $TiCl_4/TiBr_4$-mixed co-initiator is reported in this paper.

Experimental Section

Materials. Titanium tetrachloride ($TiCl_4$, Aldrich, 99.9%), titanium tetrabromide ($TiBr_4$, Aldrich, 98%), and 2,6-di-*tert*-butylpyridine (DTBP, Aldrich, 97%) were used as received. 2-Chloro-2,4,4-trimethylpentane (TMPCl) was prepared according to the literature.[5] Methyl chloride (MeCl), isobutylene (IB), hexanes (Hex), and methanol have been purified as described previously;[6] MeCl and IB were dried in the gaseous state by passing them through in-line gas-purifier columns packed with BaO/Drierite. They were condensed in the cold bath of a glovebox prior to polymerization. Hex were refluxed for 24 h with concentrated sulfuric acid, washed neutral with distilled water, dried for 48 h on molecular sieves, refluxed for 24 h, and distilled from CaH_2 under a nitrogen atmosphere. Methanol was purified by distillation.

Titanium tetrabromide is an orange solid at room temperature. At the polymerization temperature, such as −80 °C, $TiBr_4$ does not fully dissolve in MeCl or dichloromethane. However, $TiBr_4$ is soluble in $TiCl_4$ at room temperature at any ratio.[7] Therefore, $TiCl_4/TiBr_4$ mixtures with different molar ratios were prepared by mixing $TiBr_4$ and $TiCl_4$ at room temperature and cooled to the polymerization temperature.

General Polymerization Procedure. All polymerizations were carried out under a dry nitrogen atmosphere in an MBraun 150 M glovebox (Innovative Technology Inc., Newburyport, MA). Culture tubes (75 mL) were used as polymerization reactors, and the total volume of the reaction mixture was 25 mL. The polymerization mixture was quenched with excess prechilled methanol. Polyisobutylene (PIB) was recovered and purified twice by precipitation from Hex/methanol. Monomer conversions were determined by gravimetric analysis. In all experiments the volume of IB was deducted from that of hexanes; thus, the Hex/MeCl ratio indicates the (Hex + IB)/MeCl ratio. Compensating this way for the solvent polarity change upon addition of IB is especially important when high IB concentrations are used.

Example for Polymerization. In a representative experiment the polymerization was carried out in Hex/MeCl 60/40

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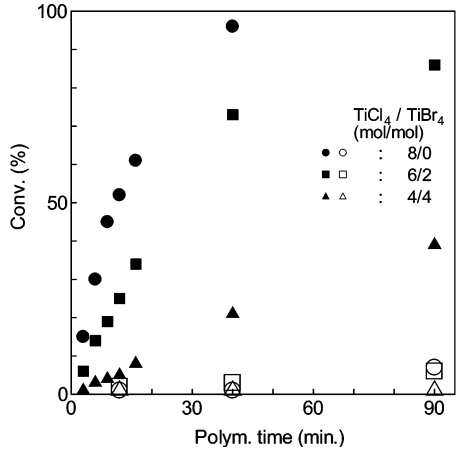


Figure 1. Conversion−time plots of polymerization of isobutylene (IB) with $TiCl_4/TiBr_4$ in the presence (filled symbol) and absence (open symbol) of 2-chloro-2,4,4-trimethylpentane (TMPCl). $[TiCl_4 + TiBr_4] = 0.036$ M, polymerization temperature = −80 °C, solvent = (Hex + IB)/MeCl = 60/40 (v/v), $[TMPCl]_0 = 0.002$ M (filled) and 0 M (open), [2,6-di-*tert*-butylpyridine, DTBP] = 0.0035 M, $[IB]_0 = 2.0$ M.

(v/v) at −80 °C using the following concentrations: [TMPCl] = 0.002 mol L^{-1}, [DTBP] = 0.0035 mol L^{-1}, [IB] = 2.0 mol L^{-1}, and $[TiCl_4 + TiBr_4] = 0.036$ mol L^{-1}. In the case of $TiCl_4/TiBr_4 = 4/4$, into a 75 mL culture tube at −80 °C, 10.1 mL of Hex, 7.0 mL of MeCl, 0.5 mL of DTBP stock solution in Hex (1.8×10^{-4} mol L^{-1}), 0.5 mL of TMPCl stock solution in Hex (1.0×10^{-4} mol L^{-1}), and 3.9 mL of IB were added and mixed thoroughly. The polymerization was started by the addition of 3.0 mL of $TiCl_4 + TiBr_4$ stock solution (3.1×10^{-4} mol L^{-1} in MeCl). After 90 min, the solution was mixed with 5 drops of prechilled methanol to quench. The polymer was precipitated twice from methanol. PIB was obtained with conversion of 39.1%, $M_n = 23\,200$ and $M_w/M_n = 1.19$.

Characterization. Molecular weights were measured at room temperature using a Waters HPLC system equipped with a model 510 HPLC pump, a model 250 dual refractometer/viscometer detector (Viscotek), a model 486 UV/vis detector, a model 712 sample processor, and five ultra-Styragel GPC columns connected in the following series: 500, 10^3, 10^4, 10^5, and 100 Å. Tetrahydrofuran was used as eluent at a flow rate of 1.0 mL/min. Molecular weight and molecular weight distribution were determined by using the universal calibration curve (Viscotek TriSEC GPC software). For structural analysis ^{1}H NMR spectroscopic measurements were carried out on a Bruker 250 MHz spectrometer.

Results and Discussion

Polymerization of IB with Different $TiCl_4/TiBr_4$ Ratio. Before studying the polymerization with $TiCl_4/TiBr_4$, direct initiation from the mixed $TiCl_4/TiBr_4$ co-initiator was studied. The time vs conversion plots for the polymerization of IB with $TiCl_4/TiBr_4$ in the presence or absence of TMPCl are shown in Figure 1. In the presence of TMPCl, the polymerization proceeds and polymer is obtained at all molar ratios of $TiCl_4/TiBr_4$. On the other hand, in the absence of TMPCl, the polymerization is extremely slow, and the conversion is less than 10% in 90 min at all molar ratios of $TiCl_4/TiBr_4$. Consequently, the polymerization initiated by cation sources other than the initiator can be neglected in this polymerization system.

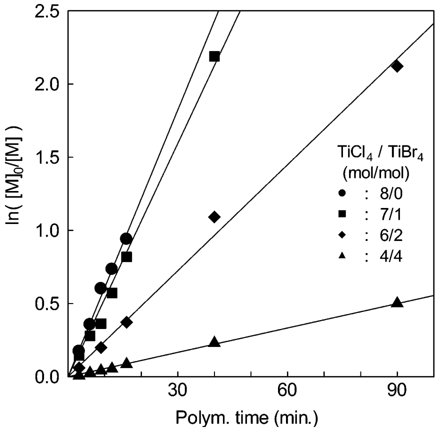


Figure 2. First-order plots of the polymerization of IB with different $TiCl_4/TiBr_4$ ratio at constant total titanium halide concentration ($[TiCl_4 + TiBr_4] = 0.036$ M). Polymerization temperature = −80 °C, solvent = (Hex + IB)/MeCl = 60/40 (v/v), [2-chloro-2,4,4-trimethylpentane, $TMPCl]_0 = 0.002$ M, [2,6-di-*tert*-butylpyridine, DTBP] = 0.0035 M, $[IB]_0 = 2.0$ M.

The first-order plots of polymerization of IB with different $TiCl_4/TiBr_4$ ratios are shown in Figure 2. Straight lines are obtained even when the $TiCl_4/TiBr_4$ molar ratio is decreased from 8/0 to 7/1, 6/2, and 4/4; thus, it appears that the concentration of the active species remains constant within the experimental time scale, and termination is not detectable. From the slope of the first-order plots, the apparent rate constants of propagation (k_{app}) for each $TiCl_4/TiBr_4$ ratio have been determined. As the $TiCl_4/TiBr_4$ molar ratio decreases, the k_{app} value decreases dramatically. The k_{app} value is represented by eq 1

$$k_{app} = k_p^{\pm}[PIB^+LA_n^-] \qquad (1)$$

where $k_p^{\pm}$ is the rate constant of propagation for ion pairs. We have already reported that $k_p^{\pm}$ is independent of nature of Lewis acid.[4] Consequently, the dramatic change in k_{app} in the polymerization of IB using $TiCl_4/TiBr_4$ originates from a drastic decrease of the concentration of ion pair, $[PIB^+Ti_2Cl_{(x+1)}Br_{(8-x)}^-]$, which in turn suggests that the Lewis acidity of $Ti_2Cl_xBr_{(8-x)}$ decreases with decreasing x.

Interestingly, k_{app} changes significantly by even a slight decrease in the $TiCl_4/TiBr_4$ ratio. This indicates that the polymerization behavior is affected dramatically by a small change in the structure of the dimeric co-initiator, $Ti_2Cl_xBr_{(8-x)}$. Since the k_{-i} values are similar (discussed later), the lower acidity influences mainly the rate constant of ionization; e.g., at −80 °C ionization with $Ti_2Cl_4Br_4$ is 14 times slower than with Ti_2Cl_8.

The conversion vs number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) plots of the obtained PIB with different $TiCl_4/TiBr_4$ ratios are shown in Figure 3. The M_n values increase linearly on the theoretical line with increased conversion, as generally encountered in living cationic polymerization, indicating the absence of chain transfer to monomer. Interestingly, the decrease of M_w/M_n values with increasing conversion is nearly identical and independent of the $TiCl_4/TiBr_4$ molar ratios. Since the M_w/M_n as a function of conversion is determined by $k_p^{\pm}[I]_0/k_{-i}$ where $[I]_0$ is the initiator concentration and k_{-i} is the rate constant of deactivation, this finding suggests similar k_{-i} values for all $TiCl_4/TiBr_4$ ratios. This is not surprising in view of the similar k_{-i} values reported for different Lewis acids.[4] A more detailed discussion follows later.

Real Co-Initiator of the Polymerization. In the polymerization of IB in conjunction with $TiCl_4$, second-order dependency in $[TiCl_4]$ has been reported, suggesting that ionization takes place by the dimer of titanium tetrachloride, Ti_2Cl_8. Thus, the polymerization rate was

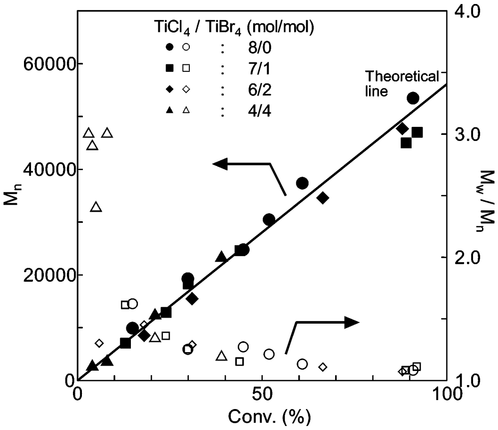


Figure 3. M_n and M_w/M_n vs conversion plots in the polymerization of IB with different $TiCl_4/TiBr_4$ ratio at constant total titanium halide concentration ($[TiCl_4 + TiBr_4] = 0.036$ M). Polymerization temperature = −80 °C, solvent = (Hex + IB)/MeCl = 60/40 (v/v), $[2\text{-chloro-}2,4,4\text{-trimethylpentane, TMPCl}]_0 = 0.002$ M, [2,6-di-*tert*-butylpyridine, DTBP] = 0.0035 M, $[IB]_0 = 2.0$ M.

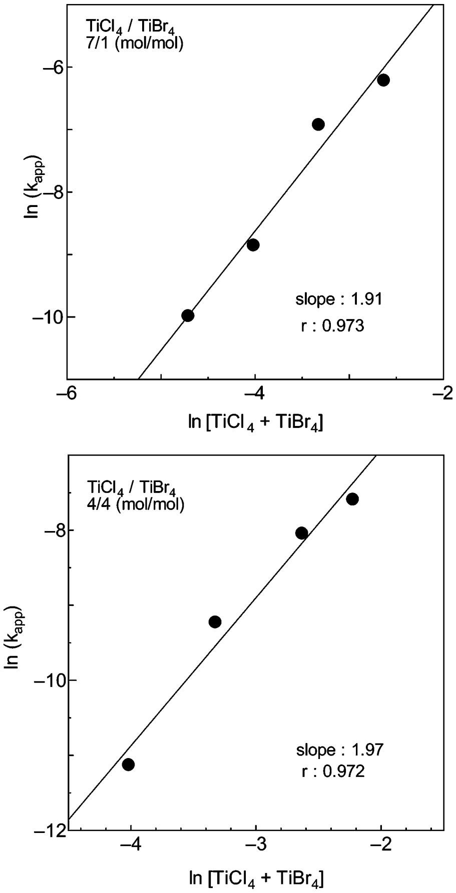


Figure 4. Bilogarithmic plots of k_{app} and $[TiCl_4 + TiBr_4]$ in the polymerization of IB with 7/1 and 4/4 (mol/mol) $TiCl_4/TiBr_4$ ratio. Polymerization temperature = −80 °C, solvent = (Hex + IB)/MeCl = 60/40 (v/v), $[2\text{-chloro-}2,4,4\text{-trimethylpentane, TMPCl}]_0 = 0.002$ M, [2,6-di-*tert*-butylpyridine, DTBP] = 0.0035 M, $[IB]_0 = 2.0$ M.

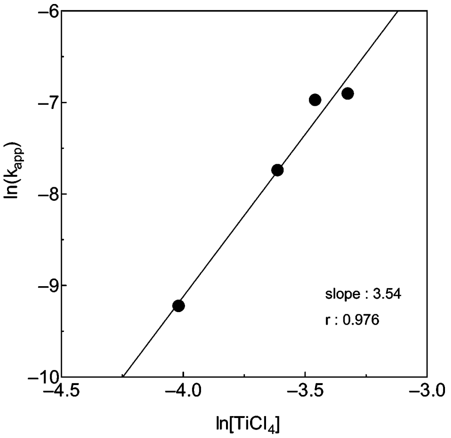


Figure 5. Bilogarithmic plots of k_{app} and $[TiCl_4]$ in the polymerization of IB with different $TiCl_4/TiBr_4$ mixtures with constant total Lewis acid concentration ($[TiCl_4 + TiBr_4] = 0.036$ M). Polymerization temperature = −80 °C, solvent = (Hex + IB)/MeCl = 60/40 (v/v), $[2\text{-chloro-}2,4,4\text{-trimethylpentane, TMPCl}]_0 = 0.002$ M, [2,6-di-*tert*-butylpyridine, DTBP] = 0.0035 M, $[IB]_0 = 2.0$ M.

studied by changing concentration of $TiCl_4 + TiBr_4$ at a constant $[TiCl_4]/[TiBr_4]$ ratio.

Using $TiCl_4/TiBr_4 = 7/1$ and 4/4 (mol/mol), the bilogarithmic plots of the k_{app} vs $[TiCl_4 + TiBr_4]$ concentration give a slope of 1.91 and 1.97, respectively, as shown in Figure 4. On the other hand, the bilogarithmic plot of k_{app} vs $[TiCl_4]$ with constant total Lewis acid concentration but with different $TiCl_4/TiBr_4$ ratio gives a slope equal to 3.54, as shown in Figure 5. It has been known that mixing $TiCl_4$ with $TiBr_4$ yields a mixed $TiCl_aBr_b$ compound. Clark et al. observed diverse $TiCl_aBr_b$ with different a and b in the Raman spectra of $TiCl_4/TiBr_4$ mixtures, indicating rapid halogen exchange.[8] Gordon et al. studied TiX_4 dimer by ab initio calculations and reported that $TiCl_4$ and $TiBr_4$ exhibit almost equal intermolecular self-interactions and similar dimerization enthalpies.[9] Accordingly, the enthalpy of ionization must be similar for the studied $TiCl_4/TiBr_4$ mixtures, which suggests similar equilibrium constants for dimerization. On the basis of these understandings, it is reasonable to consider that $TiCl_aBr_b$ with different a and b make mixed dimers, $Ti_2Cl_ABr_B$ with different A and B. The result shown in Figure 5 suggests that the dimer of $TiCl_4$, Ti_2Cl_8, is not the real co-initiator in this polymerization. The close to second-order behavior observed from the $\ln[TiCl_4 + TiBr_4]$ vs $\ln(k_{app})$ plots (Figure 4) suggests that ionization takes place by mixed $Ti_2Cl_ABr_B$.

Effect of DTBP Concentration on the Polymerization. We have previously demonstrated that the sole function of DTBP is to trap protic impurities in the $TMPCl/IB/TiCl_4$ polymerization system.[10] The effect of DTBP concentration in the polymerization of IB in conjunction with mixed $TiCl_4/TiBr_4$ Lewis acids was also studied. The first-order rate plots for the polymerization of IB using $TiCl_4/TiBr_4 = 4/4$ (mol/mol) with different DTBP concentrations are shown in Figure 6. The rate of polymerization remains unchanged in $[DTBP] = (1.7-7.0) \times 10^{-3}$ mol/L range; consequently, carbocation stabilization does not take place even in this polymerization system.

Polymerization at Different Temperatures. The polymerizations of IB with $TiCl_4/TiBr_4 = 7/1$ and 4/4 (mol/mol) were investigated at −40, −60, −70, and −80 °C. The first-order plots for various polymerization temperatures are shown in Figure 7. Using $TiCl_4/TiBr_4 = 7/1$ and 4/4 (mol/mol), straight lines were obtained at all temperatures. As the polymerization temperature increases, the rate of polymerization decreases, similarly to that already reported for the $TMPCl/IB/TiCl_4$ polymerization system.[11] Similarly to that observed for $TiCl_4$ alone, the apparent propagation rate constant k_{app}

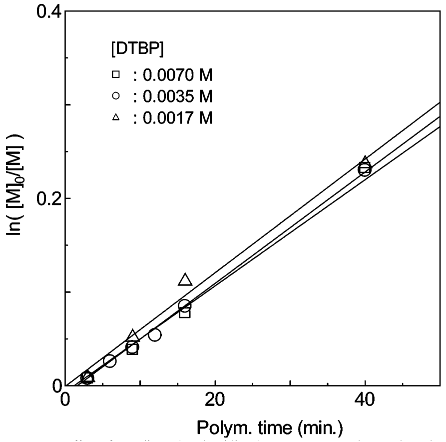


Figure 6. Effect of 2,6-di-*tert*-butylpyridine (DTBP) concentration on the polymerization of IB using $TiCl_4/TiBr_4$ (mol/mol) = 4/4 (mol/mol) as a co-initiator. $[TiCl_4 + TiBr_4] = 0.036$ M, polymerization temperature = −80 °C, solvent = (Hex + IB)/MeCl = 60/40 (v/v), [2-chloro-2,4,4-trimethylpentane, TMPCl]$_0$ = 0.002 M, [IB]$_0$ = 2.0 M.

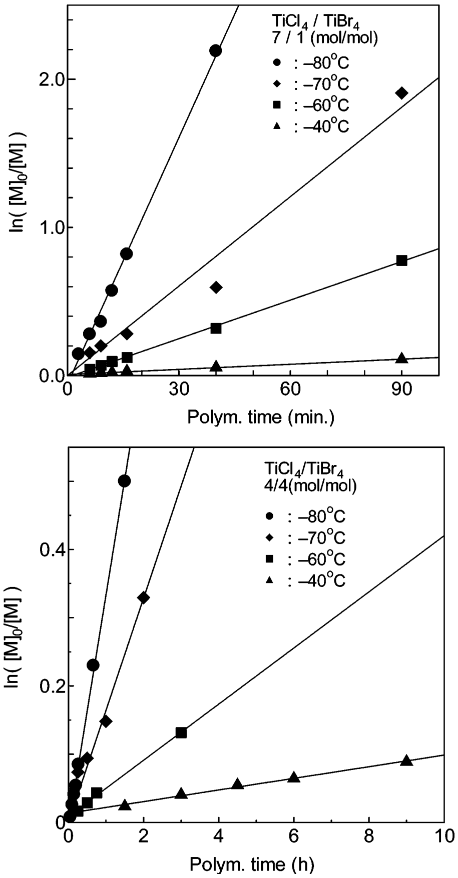


Figure 7. First-order plots of the polymerization of IB with 7/1 and 4/4 (mol/mol) mixture ratio of $TiCl_4/TiBr_4$ at different polymerization temperature. $[TiCl_4 + TiBr_4] = 0.036$ M, solvent = (Hex + IB)/MeCl = 60/40 (v/v), [2-chloro-2,4,4-trimethylpentane, TMPCl]$_0$ = 0.002 M, [2,6-di-*tert*-butylpyridine, DTBP] = 0.0035 M, [IB]$_0$ = 2.0 M.

follows the Arrhenius relationship, as shown in Figure 8. The value of k_{app} decreases drastically when the $TiCl_4/TiBr_4$ ratio decreases. The apparent activation energies (E_{app}) for the polymerization of IB using 7/1 and 4/4 (mol/mol) $TiCl_4/TiBr_4$ ratios are calculated to be −8.6 and −8.3 kcal/mol, respectively (Table 1). These values are virtually identical to the E_{app} of −8.5 kcal/mol reported for the polymerization of IB using $TiCl_4$.[11] This is not so surprising in view of the fact that the propagation of IB does not have an enthalpic barrier; therefore, the temperature only influences the equilibrium constants of ionization and Lewis acid dimerization, and the enthalpies of ionization and dimerization are similar to different $TiCl_4/TiBr_4$ mixtures.

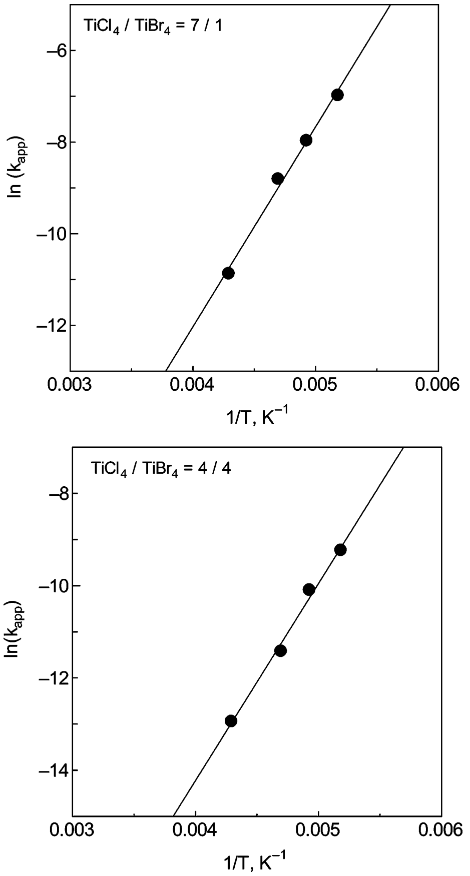


Figure 8. Arrhenius plots of the apparent first-order rate constants in the polymerization of IB with 7/1 and 4/4 (mol/mol) $TiCl_4/TiBr_4$ ratio. $[TiCl_4 + TiBr_4] = 0.036$ M, solvent = (Hex + IB)/MeCl = 60/40 (v/v), [2-chloro-2,4,4-trimethylpentane, TMPCl]$_0$ = 0.002 M, [2,6-di-*tert*-butylpyridine, DTBP] = 0.0035 M, [IB]$_0$ = 2.0 M.

End Group of Polyisobutylene Prepared with $TiCl_4/TiBr_4$. In the previous section, we concluded that the actual co-initiator in the polymerization with $TiCl_4/TiBr_4$ is the mixed dimer, $Ti_2Cl_ABr_B$. This also suggests that the polymer may contain chlorine or bromine at the chain end. To study the end group of the polymer, ^1H NMR measurements of the polymer were conducted. The ^1H NMR spectra of the polymers obtained with $TiCl_4/TiBr_4$ ratios of 8/0, 7/1, 6/2, and 4/4 are shown in Figure 9. In the case of $TiCl_4/TiBr_4$ = 8/0, the polymer obtained by drying at 80 °C for 12 h shows no peaks at the vinyl position (4.5−5.5 ppm), indicating that with this drying condition there is no dehydrochlorination at the end of the polymer. In every case, methyl and methylene groups at the polymer chloro chain end are observed at 1.72 and 1.98 ppm, respectively. With decreasing ratio of $TiCl_4/TiBr_4$, peaks **a**−**e** are observed, which are derived from exo and endo olefinic structure at the end of the polymer. The polymers obtained by $TiCl_4/TiBr_4$ = 8/0 and 7/1 do not show any peak at 1.94 ppm; on the other hand, the polymer obtained by $TiCl_4/TiBr_4$ = 4/4 shows a peak at 1.94 ppm, which is derived from methyl group in *ω*-isobutylene unit in bromine-ended PIB. These results indicate that the PIBs with

Table 1. Apparent First-Order Rate Constants (k_{app}) and Apparent Activation Energies (E_{app}) in the Polymerization of IB with $TiCl_4/TiBr_4$[a]

co-initiator	10^6k_{app}, s^{-1}, at different temp −40 °C	−60 °C	−70 °C	−80 °C	E_{app}, kcal/mol
$TiCl_4$	32	167	719	1383	−8.5
$TiCl_4/TiBr_4$ = 7/1 (mol/mol)	19	150	346	930	−8.6
$TiCl_4/TiBr_4$ = 4/4 (mol/mol)	2.4	11	41	98	−8.3

[a] k_{app} and E_{app} values in the polymerization with $TiCl_4$ are quoted from ref 11.

exo and endo structure are produced by from PIB-Br at elevated temperature such as 80 °C. The polymer dried at 55 °C for 6 h obtained by $TiCl_4/TiBr_4$ = 6/2 also showed a relatively stronger peak at 1.94 ppm. Consequently, the polymer obtained with $TiCl_4/TiBr_4$ has both chlorine and bromine end groups, and the Br end is much more sensitive than the Cl end. The weight percentages of PIB-Cl and PIB-Br are also tabulated in Table 2. The percentage of PIB-Br is the sum of percentages of exo-PIB, endo-PIB, and PIB-Br calculated from the NMR spectra.

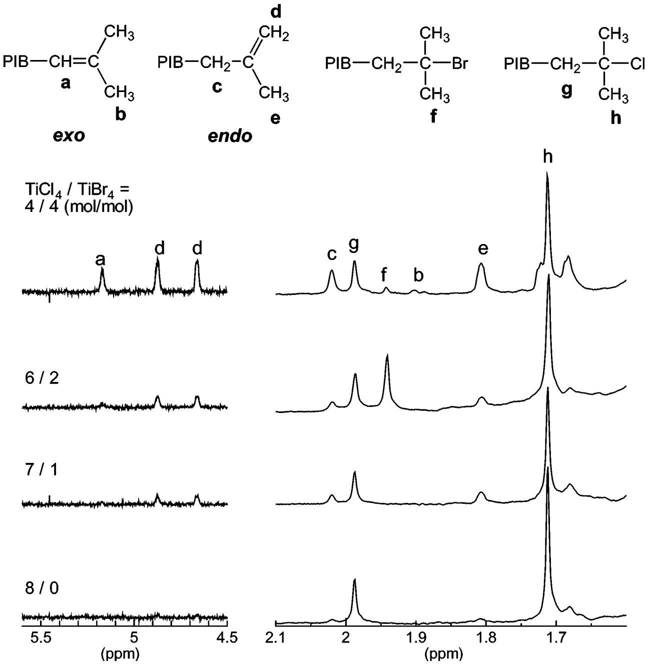


Figure 9. ^1H NMR spectra of the PIB obtained by different $TiCl_4/TiBr_4$ ratio [M_n = 7600 ($TiCl_4/TiBr_4$ = 8/0), M_n = 6000 ($TiCl_4/TiBr_4$ = 7/1), M_n = 3300 ($TiCl_4/TiBr_4$ = 6/2), M_n = 2400 ($TiCl_4/TiBr_4$ = 4/4)].

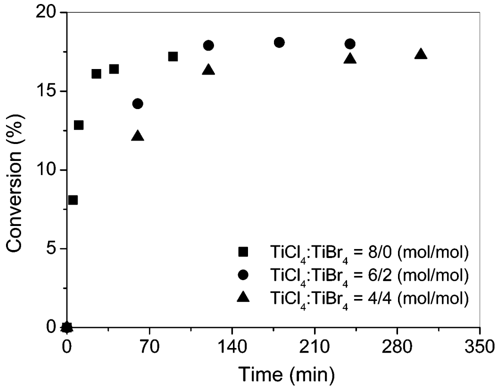


Figure 10. Time vs conversion plot in the competition experiment with [2-chloro-2,4,4-trimethylpentane, TMPCl] = 0.002 mol L^{-1}, [2,6-di-*tert*-butylpyridine, DTBP] = 0.006 mol L^{-1}, [DTE] = 0.003 mol L^{-1}, [IB] = 2.0 mol L^{-1} in Hex/MeCl 60/40 (v/v) solvent mixture at −80 °C with different [$TiCl_4$]/[$TiBr_4$] (mol/mol), where [$TiCl_4$ + $TiBr_4$] = 0.036 mol L^{-1}.

Table 2. Percentage of PIB with Chlorine End and Bromine End Calculated from NMR Analysis

$TiCl_4/TiBr_4$ (mol/mol)	mixture ratio (wt %) PIBCl	PIB(exo)	PIB(endo)	PIBBr
8/0	>99	<1	0	0
7/1	68	32	0	0
6/2	50	25	0	24
4/4	40	35	21	3

Effect of Mixed $TiCl_4/TiBr_4$ Lewis Acid Co-Initiator on the Competition Experiments of IB with 1,1-Ditolylethylene (DTE) as Capping Agent. To understand the effect of mixed Lewis acid co-initiators, competition experiments were carried out with $TiCl_4/TiBr_4$ = 8/0, 6/2, and 4/4 (mol/mol) mixed co-initiator at −80 °C in the Hex/MeCl 60/40 (v/v) solvent system. First, the time necessary to reach limiting conversion (x_∞^{IB}) was determined. Figure 10 shows the conversion vs time plots for 1,1-ditolylethylene (DTE) as capping agent. Because the strength of the Lewis acid greatly affects the concentration of the active species, the time to reach limiting conversion depends on the nature of Lewis acid. While with $TiCl_4$ the limiting conversion is reached in less than 1 h, 2 and 4 h are necessary to reach limiting conversions with $TiCl_4/TiBr_4$ = 6/2 (mol/mol) and $TiCl_4/TiBr_4$ = 4/4 (mol/mol), respectively.

The ^1H NMR spectroscopy of the obtained polymers confirmed the absence of uncapped $-\mathbf{CH_2}-C(\mathbf{CH_3})_2-Cl$ ends (absence of $\mathbf{CH_2}$ signal at 1.92 ppm and $\mathbf{CH_3}$ signal at 1.66 ppm). The molecular weights of the polymers determined by ^1H NMR spectroscopy are similar to the molecular weights determined by GPC; i.e., all chain ends were capped by the DTE using $TiCl_4/TiBr_4$ = 8/0, 6/2, and 4/4 (mol/mol) mixed co-initiator at −80 °C in the Hex/MeCl 60/40 (v/v) solvent system. The molecular weight distributions of the polymers were close to the expected most probable distribution ($M_w/M_n \sim 2$).

From the limiting conversion (x_∞^{IB}) or from the limiting number-average degree of polymerization ($DP_{n\infty}$), the rate constant ratio ($k_p^\pm/k_c^\pm$), where $k_c^\pm$ is the rate constant of the addition of DTE to PIB^+ cation, can be calculated (eqs 2 and 3).

In these equations, $[PIBCl]_0$, $[\pi Nu]_0$, and $[IB]_0$ are the initial chain end, DTE, and IB concentration, respectively.

$$\frac{k_p^\pm}{k_c^\pm} = \frac{\ln(1 - x_\infty^{IB})}{\ln(1 - [PIBCl]_0/[\pi Nu]_0)} \tag{2}$$

$$\frac{k_p^\pm}{k_c^\pm} = \frac{\ln(1 - DP_{n\infty}[PIBCl]_0/[IB]_0)}{\ln(1 - [PIBCl]_0/[\pi Nu]_0)} \tag{3}$$

The reactivity ratios were calculated from x_∞^{IB} using eq 2 and from the $DP_{n\infty}$ using eq 3. These two methods

Table 3. Limiting Molecular Weights of PIB Determined by GPC and ^{1}H NMR Spectroscopy with $TiCl_4/TiBr_4$ = 8/0, 6/2, and 4/4 (mol/mol)[a]

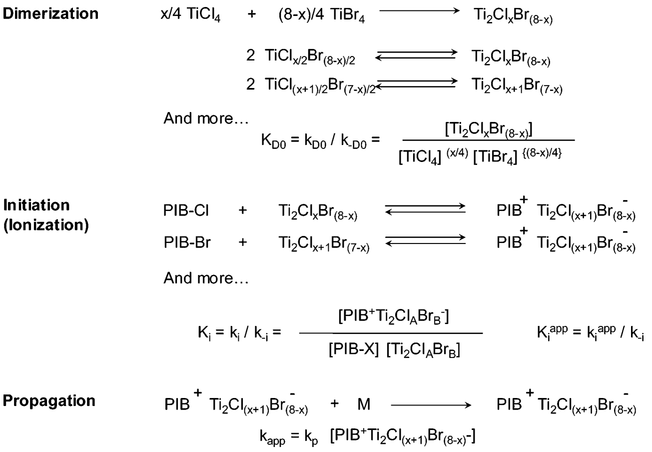
Lewis acid (mol/mol)	x_∞^{IB} (%)	$M_{n,GPC}$	M_w/M_n	$M_{n,NMR}$	$k_p^\pm/k_c^\pm$ (x_∞^{IB})	$k_p^\pm/k_c^\pm$ ($DP_{n\infty}$)	$k_p^\pm$ ($L\ mol^{-1}\ s^{-1}$)
$[TiCl_4]/[TiBr_4] = 8/0$	17.2	10 200	2.2	10 500	0.17	0.18	5.3×10^8
$[TiCl_4]/[TiBr_4] = 6/2$	17.9	10 700	2.0	11 000	0.18	0.19	5.6×10^8
$[TiCl_4]/[TiBr_4] = 4/4$	17.3	10 500	2.2	10 600	0.17	0.19	5.4×10^8

[a] $[TiCl_4 + TiBr_4] = 0.036$ mol L^{-1}, [2-chloro-2,4,4-trimethylpentane, TMPCl] = 0.002 mol L^{-1}, [2,6,-di-*tert*-butylpyridine, DTBP] = 0.006 mol L^{-1}, [1,1-ditolylethylene, DTE] = 0.003 mol L^{-1}, [IB] = 2.0 mol L^{-1} in Hex/MeCl 60/40 (v/v) at −80 °C.

Table 4. k_p, k_{-i}, K_i^{app}, and k_i^{app} Values from the Molecular Weight Distribution−Conversion Curves

ratio (mol)								
$TiCl_4$	$TiBr_4$	polym temp	β	10^6k_{app} (s^{-1})	$10^{-8}k_p$ ($L\ mol^{-1}\ s^{-1}$)	$10^{-7}k_{-i}$ (s^{-1})	$10^8K_i^{app}$ ($L^2\ mol^{-2}$)	k_i^{app} ($L^2\ mol^{-2}\ s^{-1}$)
8	0	−80	22.6	1000	5.3	2.1	73	15.3
6	2	−80	23.2	430	5.6	2.2	30	6.5
4	4	−80	18.1	98	5.4	1.7	7.0	1.2

Scheme 1. Conceivable Elementary Reactions in Dimerization, Activation−Deactivation (Ionization), and Propagation Steps in the Polymerization of IB with $TiCl_4/TiBr_4$



yielded similar $k_p^\pm/k_c^\pm$ values (Table 3). The $k_p^\pm$ values in Hex/MeCl 60/40 (v/v) solvent mixtures at −80 °C were determined from the average $k_p^\pm/k_c^\pm$ using $k_c^\pm = 3 \times 10^9$ L mol^{-1} s^{-1}, which was reported in our recent publication.[4] In agreement with our previous finding that $k_p^\pm$ is independent of the nature of Lewis acid, the $k_p^\pm$ values for various ratios of $TiCl_4/TiBr_4$ were similar to the reported value for $TiCl_4$, Me_2AlCl, and $EtAlCl_2$.[4]

Calculation of k_i^{app}, k_{-i}, K_i^{app}, and Thermodynamic Parameters from the Molecular Weight Distribution−Conversion Plots. As the ^{1}H NMR results show, the polymers prepared with $TiCl_4/TiBr_4$ contain chloride or bromide end groups. This result indicates that there are several species of co-initiator in dimerization, initiation, and propagation steps. Scheme 1 shows conceivable elementary reactions in dimerization and activation−deactivation (initiation) and propagation steps. In the dimerization steps, several species of multiple Lewis acids [$Ti_2Cl_xBr_{(8-x)}$, $Ti_2Cl_{(x+1)}Br_{(7-x)}$, and so on] have elementary dimerization reactions. These dimers ionize PIB-Cl or PIB-Br, and $Ti_2Cl_xBr_{(8-x)}$ and $Ti_2Cl_{(x+1)}Br_{(7-x)}$ are produced. In the deactivation step, $Ti_2Cl_xBr_{(8-x)}$ and $Ti_2Cl_{(x+1)}Br_{(7-x)}$ are produced again, and furthermore, other types of active counteranions may be produced when $Ti_2Cl_{(x+1)}Br_{(7-x)}$ reacts with chlorine-ended dormant species. Although the thermodynamic parameters k_{-i}, k_i^{app}, and K_i^{app} can be calculated, we have to note that these calculated parameters are average values.

The rate constant of deactivation (k_{-i}) can be determined from the molecular weight distribution−conversion (x) plot by curve fitting to eq 4 derived by Müller et al.[13]

$$\bar{M}_w/\bar{M}_n = 1 + \frac{1}{\beta}\left(\frac{2}{x} - 1\right) \tag{4}$$

In this equation $\beta = k_{-i}/([I]_0k_p^\pm)$, where $[I]_0$ is the initiator (polymer) concentration and $k_p^\pm$ is the rate constant of propagation for ion pairs. Equation 4 is valid when the fraction of active chain end $[P^+LA_nCl^-]/[I]_0$ is $\leq 10^{-2}$ and $\beta \geq 10$. The molecular weight distribution vs conversion plots obtained with $TiCl_4/TiBr_4$ 8/0, 7/1, 6/2, and 4/4 (mol/mol) at −80 °C were fitted to eq 4, and the β values were determined. Figure 11 shows $2/x - 1$ vs $(M_w/M_n) - 1$ plots obtained with the TMPCl/$TiCl_4/TiBr_4$ initiator system in Hex/MeCl 60/40 (v/v) solvent mixture at −80 °C. The correlation between the fitted line and the experimental points is excellent with different $TiCl_4/TiBr_4$ ratios. The β values of 22.6, 24.3, 23.2, and 18.1 were obtained for $TiCl_4/TiBr_4$ 8/0, 7/1, 6/2, and 4/4 (mol/mol), respectively. In the previous section, we reported that $k_p^\pm$ (= (5.3−5.6) × 10^8 L mol^{-1} s^{-1}) is independent of the ratio of $TiCl_4$ and $TiBr_4$. Thus, from β and the known value of $k_p^\pm$ the value of k_{-i} can be calculated. The β values are independent of the $TiCl_4/TiBr_4$ ratio, indicating that the rate constant of deactivation is independent of the ratio of $TiCl_4/TiBr_4$, since $k_p^\pm$ is constant.

The apparent equilibrium constant of ionization (activation) K_i^{app} (= K_iK_{D0}, where K_i is the absolute equilibrium constant of ionization and K_{D0} is the equilibrium constant of $TiCl_4/TiBr_4$ dimerization) is expressed as

$$K_i^{app} = \frac{[P^+TiCl_ABr_B^-]}{[PIB-X][TiCl_4 + TiBr_4]^2} \tag{5}$$

where $[P^+TiCl_ABr_B^-]$ is the concentration of active center, [PIB−X] is the concentration of initiator, and $[TiCl_4 + TiBr_4]$ is the total concentration of co-initiator. The K_i^{app} value can be calculated from the absolute $k_p^\pm$ and the apparent propagation rate constant k_{app}. The apparent value of k_i ($k_i^{app} = k_iK_{D0}$, where k_i is the absolute rate constant of ionization) is expressed as

$$k_i^{app} = k_{-i}K_i^{app} \tag{6}$$

From the calculated K_i^{app} and k_{-i}, the k_i^{app} value can also be obtained.

Table 4 summarizes the calculated k_{app}, k_i^{app}, k_{-i}, and K_i^{app} values obtained with the TMPCl/$TiCl_4/TiBr_4$ ini-

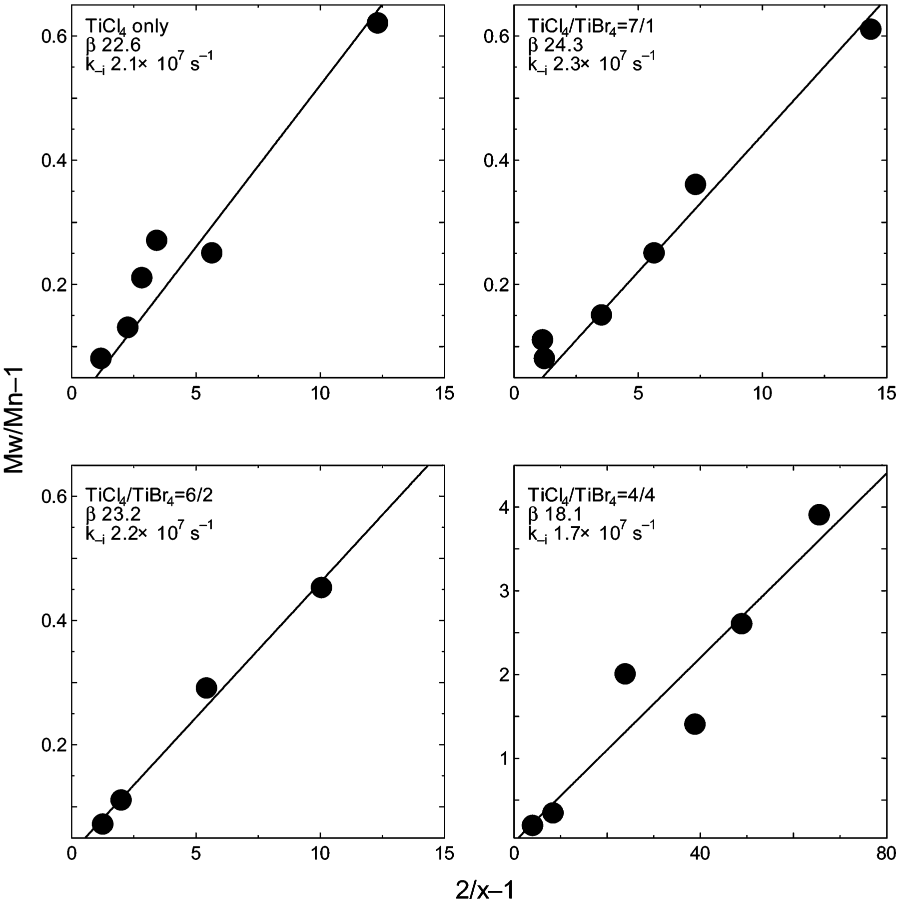


Figure 11. Molecular weight distribution (M_w/M_n)−conversion (x) plots at different $TiCl_4/TiBr_4$ ratio. [$TiCl_4$ + $TiBr_4$] = 0.036 M, solvent: (Hex + IB)/MeCl = 60/40 (v/v), [2-chloro-2,4,4-trimethylpentane, TMPCl]$_0$ = 0.002 M, [2,6,-di-*tert*-butylpyridine, DTBP] = 0.0035 M, [IB]$_0$ = 2.0 M.

tiator system. At −80 °C, k_{app} decreases when the ratio of $TiCl_4/TiBr_4$ decreases due to lower Lewis acidity of $TiCl_4/TiBr_4$ compared to that of $TiCl_4$. The k_{app} also decreases with increasing polymerization temperature, which is a generally observed trend in the polymerization of IB. The k_{-i} values obtained with $TiCl_4/TiBr_4$ = 8/0, 7/1, 6/2, and 4/4 and that reported for other polymerization systems ($k_{-i} = 10^7-10^8\ s^{-1}$) are virtually identical. The similar k_{-i} values obtained with various $TiCl_4/TiBr_4$ ratios indicate that the effect nature of Lewis acid on the deactivation step is small. The K_i^{app} decreases with decreasing $TiCl_4/TiBr_4$ ratio. This trend is the result of the close to constant k_{-i} value and decreasing k_i^{app} with decreasing $TiCl_4/TiBr_4$ ratio. Accordingly, the enthalpy of ionization must be similar for the studied $TiCl_4/TiBr_4$ mixtures,[9] which suggests similar equilibrium constants for dimerization (K_{D0}).

Conclusions

A small change in the structure of the co-initiator drastically alters the Lewis acidity and thereby the polymerization rate. The polymerization of IB using $TiCl_4/TiBr_4$ mixed Lewis acids proceeds in a living fashion, but the polymerization rate decreases with decreasing $TiCl_4/TiBr_4$ ratio. The polymerization rate is independent of the concentration of proton trap. The active co-initiator in this polymerization system is the mixed dimer, $Ti_2Cl_xBr_{(8-x)}$, not the dimer of $TiCl_4$ or $TiBr_4$. By the stepwise replacement of Cl to Br, the Lewis acidity decreases, which results in a decreased ionization rate constant while the deactivation rate constant remains essentially unchanged. Therefore, the decreasing overall rates of polymerization with decreasing $TiCl_4/TiBr_4$ ratio are exclusively due to the lower equilibrium constant of ionization, which results in lower concentration of ion pairs, $[PIB^+Ti_2Cl_{(x+1)}Br_{(8-x)}^-]$.

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