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Quasiliving Carbocationic Polymerization. V. Quasiliving Polymerization of Indene

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ABSTRACT

Quasiliving polymerization of indene, i.e., an increase of the molecular weight of polyindenes with the cumulative amount of consumed monomer, has been demonstrated using the "H_2O"/BCl_3, 2-chloroindene/BCl_3, "H_2O"/$TiCl_4$, 2-chloroindene/$TiCl_4$, and cumyl chloride/$TiCl_4$ initiating systems in CH_2Cl_2 solvent at -50°C. However, chain transfer operates in every system investigated, and sets a limit to $\overline{DP}_{n,max}$. The efficiency of the 2-chloroindene and cumyl chloride initiators is very low. The behavior of BCl_3 and $TiCl_4$ coinitiators on the polymerization has also been investigated.

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INTRODUCTION

The quasiliving polymerization of isobutylene has been discussed in detail [1]. Though the number-average molecular weights of polyisobutylenes increased with the cumulative amount of consumed monomer, controlled initiation could not be obtained with the initiating systems employed, i.e., "H_2O"/BCl_3, "H_2O"/$TiCl_4$, cumyl chloride/$TiCl_4$. In the presence of the cumyl chloride/$TiCl_4$ initiator system, most probably two propagating ion pairs are operational: $\sim\!\sim C^{\oplus}(CH_3)_2TiCl_4OH^{\ominus}$ and $\sim\!\sim C^{\oplus}(CH_3)_2TiCl_5^{\ominus}$. The first ion pair is formed in the presence of "H_2O" (impurities) in the system whereas the second one arises from the cumyl chloride initiator. Since in most polymerizations chain transfer to monomer was found to operate, investigations were extended to monomers thought to be less prone to chain transfer than isobutylene.

This paper concerns the quasiliving polymerization of indene using the continuous monomer addition technique and the "H_2O"/$TiCl_4$, "H_2O"/BCl_3, 2-chloroindane/$TiCl_4$, 2-chloroindane/BCl_3, and cumyl chloride/$TiCl_4$ initiating systems in methylene chloride solvent at -50°C. Indene was selected for these investigations because irreversible chain transfer through indane-skeleton formation (which plays an important role in the polymerization of styrene derivatives) was thought to be unlikely with this monomer.

EXPERIMENTAL

Materials

Indene was stirred with 6 N HCl overnight, washed with distilled water, refluxed with 40% NaOH for 2 h, washed with distilled water, dried over molecular sieves (3Å), and fractionated from CaH_2 under vacuo three times. Purity was checked by GC. 2-Chloroindene (CI) was prepared from purified indene by hydrochlorination and purified with vacuum distillation. α-Methylstyrene was purified as described [2]. Cumyl chloride (CC) was prepared from purified α-methylstyrene by hydrochlorination; the excess HCl was removed by repeated freeze-drying. Methylene chloride was purified as described [3]. BCl_3 was condensed from a lecture bottle under N_2. $TiCl_4$ was distilled from P_2O_5 under N_2.

Procedures

Polymerizations were carried out in a stainless steel enclosure under dry N_2 at -50°C in 300 cm^3 three-neck round-bottom flasks equipped with stirrer, Teflon plug for monomer addition, and outlet for sampling. The initial volume of the charge (solvent) was 100 cm^3. Monomer was fed continuously be a precision metering pump (Beckman Model 110 A) through a precision capillary outlet.

Samples (0.1 cm^3) were withdrawn with a syringe from the reaction mixture and were injected into capped vials containing excess methanol. Polymerizations were stopped by adding methanol to the reaction mixture. Conversions were determined gravimetrically.

Molecular weights were determined by a Waters Associates High Pressure GPC equipped with four Microstyragel columns (10^5, 10^4, 10^3, and 500 Å) and UV and RI detectors. Molecular weights were calculated from a calibration curve obtained with polystyrene standards.

RESULTS AND DISCUSSION

Polymerization with the "H_2O"/BCl_3 Initiating System

Three experiments have been carried out with the "H_2O"/BCl_3 initiating system using continuous monomer addition. Data are listed in Table 1. $\overline{DP}_{n,max}$ and $[I]_0$ values were calculated using the following equation:

$$[P] = \frac{At\xi}{\overline{DP}_n} = [I]_0 + \frac{1}{\overline{DP}_{n,max}} At\xi \qquad (1)$$

where [P] is the total number of polymer molecules, A is the monomer input rate, and ξ is the conversion; thus $At\xi$ stands for the amount of monomer consumed during time t. $\overline{DP}_{n,max} = k_p/k_{tr}$, as usual. Figure 1 is a plot of [P] versus $At\xi$, and the linearity of the data suggest a QL_{R1} system, i.e., a system with irreversible chain transfer by our classification [4].

Most probably due to the slow polymerization of indene with the "H_2O"/BCl_3 initiating system, conversions were less than 100%. The GPC traces of two representative samples are shown in Fig. 2. Evidently the molecular weight of polyindene increases with the cumulative weight of consumed monomer; however, due to chain transfer the number of polymer molecules increases during polymerization (Fig. 1). $\overline{DP}_{n,max}$ is highest with 490 at the optimum addition rate ($A = 4.3 \times 10^{-3}$ mol/min). Lower $\overline{DP}_{n,max}$ values have been obtained both at higher and lower addition rates ($A = 17.2 \times 10^{-3}$ mol/min, $\overline{DP}_{n,max} = 305$; $A = 0.34 \times 10^{-3}$ mol/min, $\overline{DP}_{n,max} = 306$).

TABLE 1. Polymerization of Indene with "H_2O"/BCl_3 Initiating System Using Continuous Monomer Addition[a]

Sample	t (min)	Cumulative amount of consumed monomer $At\xi$ (mol $\times 10^3$)	$\overline{M}_n$ $\times 10^{-3}$	$\overline{DP}_n$ $\times 10^{-2}$	[P] (mol $\times 10^4$)	$\overline{M}_w/\overline{M}_n$	$\overline{DP}_{n,max}$, calculated	$[I]_0$ calc (mol $\times 10^4$)	Final conversion
		A = 17.2×10^{-3} mol/min (dilute monomer: 50 vol% monomer + 50 vol% CH_2Cl_2)							
KK 14	2	19.2	18.2	1.57	1.25	1.9			57% (ξ = 0.57)
15	4	39.2	23.1	1.99	1.97	2.2			
16	6	58.8	24.6	2.11	2.79	2.1	305	0.67	
17	8	78.5	29.8	2.57	3.05	1.9			
18	10	98.0	28.9	2.49	3.93	1.9			
		A = 4.3×10^{-3} mol/min (dilute monomer: 25 vol % monomer + 75 vol% CH_2Cl_2)							
KK 1	9	27.5	21.9	1.89	1.46	2.2			71% (ξ = 0.71)
2	15	45.8	33.1	2.85	1.61	1.8			
3	20	61.1	39.8	3.43	1.78	1.7			
4	25	76.3	39.0	3.36	2.27	1.7	490	0.73	
5	30	91.6	39.8	3.43	2.67	1.8			
6	35	106.9	43.7	3.76	2.84	1.7			
7	40	122.1	42.6	3.67	3.33	1.4			
		A = 0.34×10^{-3} mol/min (dilute monomer: 10 vol% monomer + 90 vol% CH_2Cl_2)							
OO 6	50	11.4	16.5	1.42	0.80	1.8			65% (ξ = 0.65)
7	100	22.8	23.8	2.05	1.11	1.8			
8	150	34.2	26.0	2.24	1.53	1.8	306	0.43	
9	200	45.6	25.8	2.15	2.12	1.8			
10	250	57.0	30.7	2.64	2.16	1.8			

[a] $[BCl_3]_0 = 2.5 \times 10^{-2}$ mol/dm^3, T = -50°C, $V_0 = 100$ cm^3.

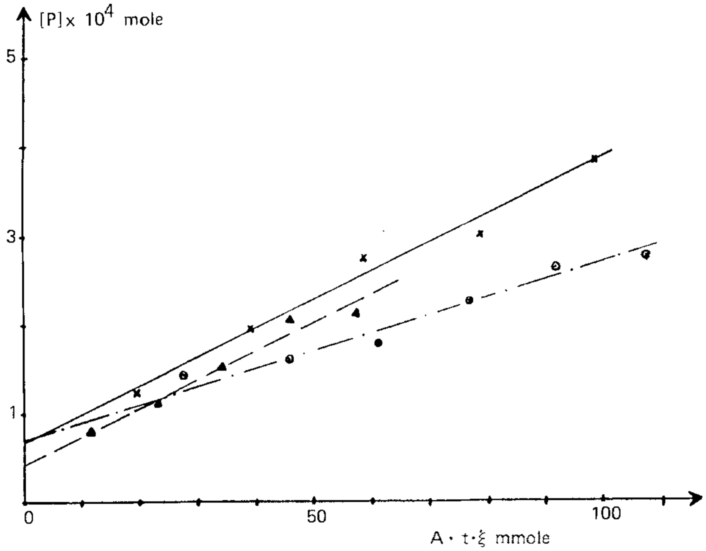

FIG. 1. Number of polymer molecules [P] versus cumulative amount of consumed monomer (Atξ) plot at different monomer addition rates (×, 17.2; ⊗, 4.3; △, 0.34 mmol/min). Initiating system: "H_2O"/BCl_3.

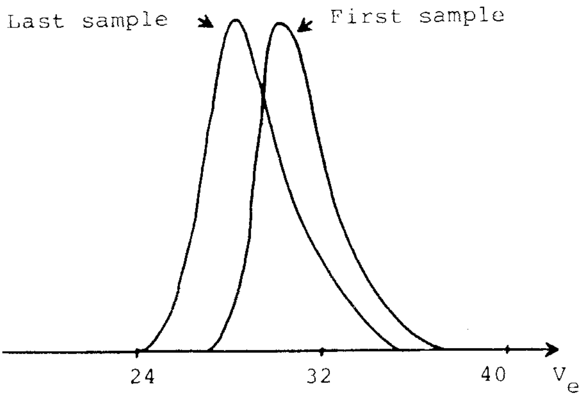

FIG. 2. GPC traces of polyindene samples prepared with "H_2O"/ BCl_3 initiating system using continuous monomer addition.

TABLE 2. Polymerization of Indene with the "H_2O"/$TiCl_4$ Initiating System Using Continuous Monomer Addition[a]

Sample	t (min)	Cumulative amount of consumed monomer At ξ (mol $\times 10^3$)	$\overline{M}_n \times 10^{-3}$	$\overline{DP}_n \times 10^{-2}$	[P] (mol $\times 10^4$)	$\overline{M}_w/\overline{M}_n$	$\overline{DP}_{n,max}$, calculated	$[I]_0$ calc (mol $\times 10^4$)
		A = 4.3 × 10^{-3} mol/min (dilute monomer: 25 vol% monomer + 75 vol% CH_2Cl_2)						
NN 1-5 No molecular weight increase			70	603		1.7		
		A = 2.1 × 10^{-3} mol/min (dilute monomer: 12.5 vol% monomer + 87.5 vol% CH_2Cl_2)						
NN 11	8	17.2	41.5	3.57	0.48	1.97	630	0.22
12	16	34.4	52.5	4.52	0.76	1.80		
13	24	51.6	51.8	4.46	1.00	1.66		
14	32	68.8	62.8	5.27	1.10	1.85		
15	40	86.0	63.5	5.47	1.57			
		A = 0.34 × 10^{-3} mol/min (dilute monomer: 10 vol% monomer + 90 vol% CH_2Cl_2)						
OO 1	50	17	21.4	1.84	0.92	2.10		
2	100	34	24.9	2.14	1.59	1.98		
3	150	51	28.9	2.49	2.05	2.00	365	0.6
4	200	68	31.9	2.69	2.53	1.98		
5	250	85	35.5	3.06	2.78	1.95		

[a] Final conversion is 100% (ξ = 1) in every case, $[TiCl_4]_0 = 2.5 \times 10^{-2}$ mol/dm^3, T = 50°C, $V_0 = 100$ cm^3.

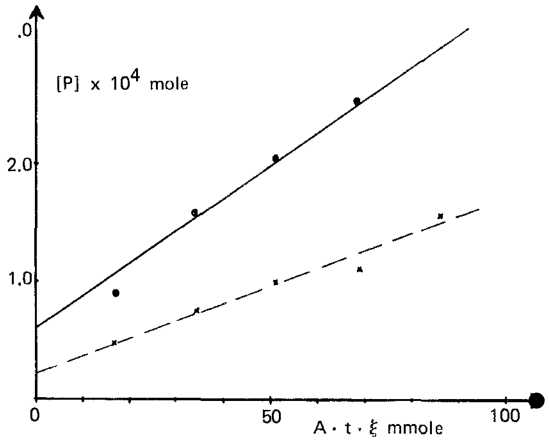

FIG. 3. [P] versus Atξ plot at different monomer addition rates (×, 2; ⊙, 0.34 mmol/min). Initiating system: "H_2O"/$TiCl_4$.

A similar, though more pronounced phenomenon has been described in conjunction with styrene derivatives [2, 5] where highest $\overline{DP}_{n,max}$ values were obtained at an optimum addition rate. It was postulated that a relatively high monomer addition rate, chain transfer to monomer depresses $\overline{DP}_{n,max}$, while at relatively low monomer addition rate, indane formation operates. Chain transfer involving the formation of an indane skeleton by intramolecular alkylation of a phenyl ring would be quite unfavorable because of the very rigid polyindene structure. However, chain transfer to moisture impurities in the system may occur.

Polymerization with the "H_2O"/$TiCl_4$ Initiating System

A series of experiments have been carried out with the "H_2O"/$TiCl_4$ initiating system using continuous monomer addition. Data are listed in Table 2. Conversions were 100% in every case (ξ = 1.0). Evidently the polymerization of indene is faster with "H_2O"/$TiCl_4$ than with the "H_2O"/BCl_3 initiating system. Molecular weight growth has not been obtained at an addition rate of A = 4.3×10^{-3} mol/min and the $\overline{DP}_n$'s of samples remained at ~600. By decreasing the addition rate to A = 2.1×10^{-3} mol/min, the molecular weights increased with monomer input, yielding $\overline{DP}_{n,max}$ = 630. Using an even lower addition rate, A = 0.43×10^{-3} mol/min, the $\overline{DP}_{n,max}$ decreased

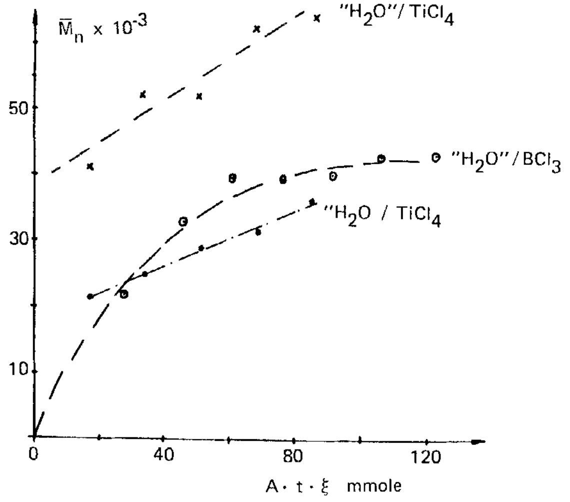

FIG. 4. The effect of coinitiator on $\overline{M}_n$ versus Atξ curves.

to 365. Figure 3, a plot of [P] versus monomer input constructed from the data in Table 2, indicates the presence of chain transfer in the system, i.e., a QL_{R1} system by our classification [4]. Figure 4 shows the dependence of molecular weight on the cumulative amount of consumed monomer in the presence of "H_2O"/BCl_3 and "H_2O"/$TiCl_4$ initiating systems. The initial jump in the $\overline{M}_n$'s obtained with "H_2O"/$TiCl_4$ has also been observed with the isobutylene/"H_2O"/$TiCl_4$ system. Similarly to the isobutylene system [1], the $\overline{M}_n$'s did not increase when the monomer addition rate was relatively high (A = 4.3×10^{-3} mol/min).

According to Fig. 4, the $\overline{M}_n$ versus Atξ curve obtained with the "H_2O"/BCl_3 initiating system shows a slower initial increase than the "H_2O"/$TiCl_4$ system. Evidently subtle differences exist between the behavior of "H_2O"/BCl_3 and "H_2O"/$TiCl_4$ than with "H_2O"/BCl_3, conceivably because in the presence of the less stable $BCl_3OH^\ominus$ (and $BCl_4^\ominus$) counteranion(s), ion pair collapse and reinitiation occur more frequently than with the relatively more stable $TiCl_4OH^\ominus$ (and $TiCl_5^\ominus$) counteranion. Also, initiation is most likely faster with "H_2O"/$TiCl_4$ than with "H_2O"/BCl_3, causing the initial "flash" polymerization. The collapse of the propagating ion/counterion pair is visualized as

(2)

TABLE 3. Polymerization of Indene with 2-Chloroindene/TiCl₄, 2-Chloroindene/BCl₄, and Cumyl Chloride/TiCl₄ Initiating Systems Using Continuous Monomer Addition[a]

Sample	t (min)	Cumulative amount of consumed monomer Atξ (mol $\times 10^3$)	$\overline{M}_n \times 10^{-3}$	$\overline{DP}_n \times 10^2$	[P] (mol $\times 10^4$)	$\overline{M}_w/\overline{M}_n$	$\overline{DP}_{n,max}$ calculated	$[I]_0$ calc (mol $\times 10^4$)	Final conversion
		$[I]_0 = 0.98 \times 10^{-2}$ mol/dm^3, CI, $[TiCl_4]_0 = 3.5 \times 10^{-2}$ mol/dm^3							
RR 2	5	21.5	16.7	1.44	1.40	3.75	359	1.04	100%
3	10	43	20.0	1.72	2.34	2.80			(ξ = 1)
4	15	64.5	24.6	2.12	2.85	2.3			
5	20	86	28.9	2.49	3.23	2.3			
6	25	107.5	31.1	2.68	3.76	2.0			
		$[I]_0 = 0.98 \times 10^{-2}$ mol/dm^3, CI, $[BCl_3] = 3.6 \times 10^{-2}$ mol/dm^3							
RR 12	4	17.2	13.1	1.13	1.52	1.80	359	1.03	80%
13	8	34.4	18.9	1.63	2.11	2.0			(ξ = 0.8)
14	12	51.6	23.7	2.00	2.75	2.0			
15	16	68.8	29.4	2.50	2.75	2.0			
16	20	86.0	29.4	2.50	3.44	2.0			
		$[I]_0 = 1.36 \times 10^{-2}$ mol/dm^3, CC, $[TiCl_4]_0 = 2.5 \times 10^{-2}$ mol/dm^3							
NN 16	10	43	20.8	1.79	2.40	4.1	353	1.3	100%
17	20	86	31.6	2.72	3.16	3.7			(ξ = 1)
18	30	129	29.6	2.55	5.06	3.7			
19	40	172	28.3	2.43	7.08	3.3			
20	50	215	38.4	3.7	6.52	2.9			

[a] $A = 4.3 \times 10^{-3}$ mol/min, $T = -50°C$, $V_0 = 100$ cm^3.

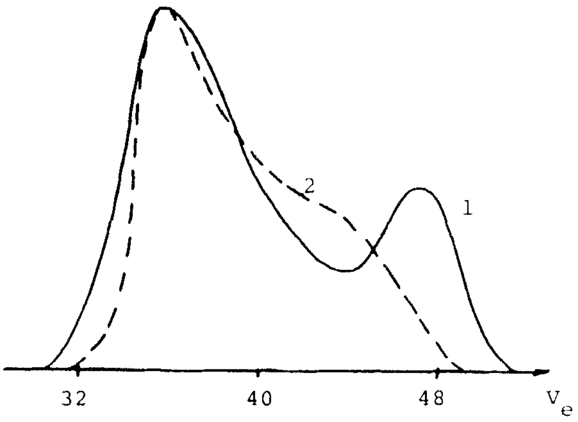

FIG. 5. GPC traces of polyisobutylene (1) and polyindene (2) samples obtained with cumyl chloride/$TiCl_4$ and 2-chloroindane/$TiCl_4$ initiating systems, respectively, using continuous monomer addition.

Reinitiation proceeds with the excess Lewis acid present in the system and is expected to be faster with $TiCl_4$ than with BCl_3.

Polymerization of Indene with the CI/BCl_3, CI/$TiCl_4$, and CC/$TiCl_4$ Initiating Systems

A series of experiments have been carried out with the CI/$TiCl_4$, CI/BCl_3, and CC/$TiCl_4$ initiating systems using continuous monomer addition. Data are summarized in Table 3. Figure 5 shows the GPC traces of polyisobutylene prepared with the CC/$TiCl_4$ initiating system [1] and that of polyindene prepared by the CI/$TiCl_4$ initiating system. The similarity between the two systems if apparent. Conceivably, in the presence of $TiCl_4$ coinitiator and a benzylic chloride initiator, "H_2O" impurities will also function as initiating species and will give rise to two propagating entities: $\sim\!\sim C^{\oplus}\ TiCl_5^{\ominus}$ and $\sim\!\sim C^{\oplus}\ TiCl_4OH^{\ominus}$, i.e., the former arising from the purposely added chlorine-containing initiators (CC or CI) and the latter arising from moisture impurities. It appears that the latter counteranion is more stable than the former. Due to high propagation rates in the presence of $TiCl_4$-based initiating systems, monomer concentrations may be locally high before perfect mixing of monomer is reached. In the presence of $TiCl_4OH^{\ominus}$, polymerization will be faster and termination [i.e., collapse of the growing $\sim\!\sim C^{\oplus}(CH_3)_2 + TiCl_4OH^{\ominus}$ ion pair to $\sim\!\sim C(CH_3)_2Cl + TiCl_3OH$] slower than with $TiCl_5^{\ominus}$. With perfect mixing and slow monomer addition this difference would vanish since the collapse of the ion pair leads to a chlorine terminus even with

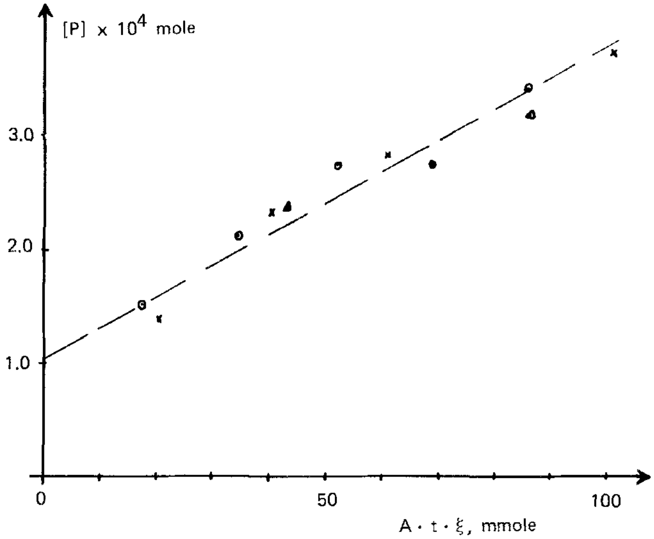

FIG. 6. Number of polymer molecules versus the cumulative amount of consumed monomer in the polymerization of indene using continuous monomer addition. Initiating system: (×) CI/$TiCl_4$, (⊙) CI/BCl_3, (△) CC/$TiCl_4$.

$TiCl_4OH^\ominus$. With the CI/BCl_3 initiating system, polymerization is slower (conversion is 80%, see Table 3) and the GPC traces of the samples are monomodal.

Figure 6 is a plot of the number of polymer molecules versus the cumulative amount of monomer consumed. The operational presence of irreversible chain transfer is indicated by the fact that [P] increases linearly with Atξ during the polymerization, i.e., a QL_{R1} system by our classification [4].

$\overline{DP}_{n,max}$ and $[I]_0$ values have been calculated by using Eq. (1). According to the calculated $[I]_0$ values (for RR 2-6, 1.03×10^{-3} mol/dm^3; for RR 12-16, 1.03×10^{-3} mol/dm^3; and for NN 16-20, 1.3×10^{-3} mol/dm^3) the initiator efficiencies are very low (< 10%). $\overline{DP}_{n,max}$ values are identical and close to those of polyidenes prepared with the "H_2O"/BCl_3 and "H_2O"/$TiCl_4$ initiating systems. Chain transfer may be due to moisture present in and/or brought into the system by continuous monomer feeding. It is possible that chain transfer could be eliminated by increasing $[I]_0$; in the case of CC/$TiCl_4$/iC_4H_9, chain transfer was virtually eliminated by increasing $[I]_0$ to 1×10^{-2} mol/dm^3 while at $[I]_0 \sim 1 \times 10^{-3}$, i.e., at initiator concentrations close to that of the water impurity level, chain transfer occurred. Further investigations are necessary to elucidate this point.

In sum, quasiliving polymerization of indene with the "H_2O"/BCl_3, CI/BCl_3, "H_2O"/$TiCl_4$, CI/$TiCl_4$, and CC/$TiCl_4$ systems can be obtained, i.e., the number-average molecular weight of polyindene increases with the cumulative amount of consumed monomer. However, chain transfer operates in every system and limits $\overline{M}_{n,max}$ values.

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