Living Carbocationic Polymerization. 55. Living Polymerization of Indene

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ABSTRACT: The cationic polymerization of indene (In) has been investigated using the 2-chloro-2,4,4-trimethylpentane (TMPCl)/$TiCl_4$ initiating system and a methyl chloride–methylcyclohexane solvent mixture at -80 °C. According to kinetic studies, initiation is slow relative to propagation. The quantitative treatment of slow initiation in living carbocationic polymerization applied to this system led to the conclusion that this polymerization is living and the rate-determining step is cationation. Functionality analysis by a chloride-selective electrode indicates that the end groups of polyindene (PIn) are secondary chlorines. The electron donors, *N*,*N*-dimethylacetamide (DMA) and hexamethylphosphoramide (HMPA), do not affect the polymerizations.

Introduction

Prior to the synthesis of polyindene–polyisobutylene–polyindene triblocks we wanted to find conditions for the living polymerization of In by the TMPCl/$TiCl_4$ initiating system. The quasiliving polymerization of In has been demonstrated earlier by the use of H_2O/BCl_3, $H_2O/TiCl_4$, 2-chloroindene/BCl_3, 2-chloroindene/$TiCl_4$, and cumyl chloride/$TiCl_4$ initiating systems and CH_2Cl_2 solvent at -50 °C.[1] However, chain transfer operated in the previous systems and set a limit to $\bar{M}_n$.

Recently, the TMPCl/$TiCl_4$ initiating system in conjunction with an electron donor was demonstrated to yield living isobutylene (IB) polymerization.[2] We decided to use the same initiating system because the TMP^+ mimics the growingPIB^+ chain[3] and would model the critical $PIB^+ + In \rightarrow PIB\text{-}In^+$ crossover.

Experimental Section

Materials. High-purity IB and methyl chloride (Linde) were dried by passing the gases through columns packed with BaO and condensing under a dry N_2 atmosphere. The synthesis and purification of TMPCl has been described.[4] $TiCl_4$ (Aldrich) was distilled from CaH_2 on the day of the experiment. Methylcyclohexane (MCHx) (Aldrich) was distilled from CaH_2. The purification of In (Aldrich) has been described,[5] and its purity (~99.7%) was determined by GC. 2,6-Di-*tert*-butylpyridine (D*t*BP), *N*,*N*-dimethylacetamide (DMA), hexamethylformamide (HMPA), $CDCl_3$ (Aldrich), methanol, and THF (Fisher) were used as received.

Polymerization. Polymerization was carried out in large culture tubes (~75 mL) in a drybox.[6] The moisture level in the charge was monitored by carrying out control experiments (in the absence of TMPCl initiator). Most of the experiments were carried out by the conventional "all monomer in (AMI)" technique.[6] In some experiments "the incremental monomer addition (IMA)" technique[6] was also used. The details of these techniques have been described.[6]

Table I
Homopolymerization of Indene[a]

no.	W_p (g)	$\bar{M}_n$ expt	$\bar{M}_n$ theo	$\bar{M}_w/\bar{M}_n$	I_{eff} (%)	[N] × 10^4
1	0.2430	7 200	1900	2.48	26	13.5
2	0.4305	10 800	3400	2.82	31	15.9
3	0.6153	13 450	4800	2.74	35	18.3
4	0.7618	14 600	5950	2.97	40	20.9
5[b]	0.1069	15 000		2.00		2.8

[a] Reaction conditions: [TMPCl] = 5.12×10^{-3} M; [$TiCl_4$] = 0.0819 M; CH_3Cl/MCHx = 40/60 (v/v); V_0 = 25 mL; 6 min; AMI method. V_0 = total volume; W_p = yield; $I_{eff} = N/I_0$ ($N = W_p/\bar{M}_n$; I_0 = moles of initiator); expt = experimental; theo = theoretical. Conversions = 100%. [b] Control experiment (absence of TMPCl).

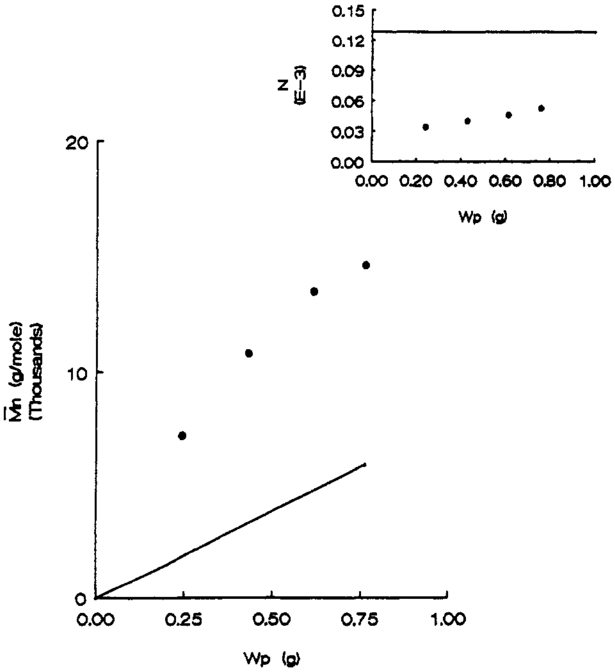

Figure 1. Number-average molecular weights ($\bar{M}_n$) and the number of polymer chains (N) as a function of the weight of PIn formed (W_p). Experimental conditions are given in Table I; solid lines are theoretical (assuming I_{eff} = 100%).

Characterization. Molecular weights and molecular weight distributions were determined by GPC (Waters high-pressure instrument, Model 6000A pump), using a series of μ-Styragel columns (100, 500, 10^3, 10^4, and 10^5 Å), a differential refractometer (Model 410), and a UV detector (Model 410), using polystyrene (PSt) calibration. The purity of In was checked by GC (Perkin-Elmer instrument, Model 8410). The [Cl^-] was determined by a chloride-selective electrode (Orion 9617 U) in combination with a Orion PH-ISE meter (SR-720). Details of the chlorine content determination method have been published.[7] ^1H NMR and ^{13}C NMR spectra were obtained using a Varian Gemini 200-MHz spectrometer and $CDCl_3$ solutions. Glass transition temperatures were determined by a Du Pont 910 DSC module with a Du Pont 9900 computer/thermal analyzer, at a heating rate of 10 °C/min.

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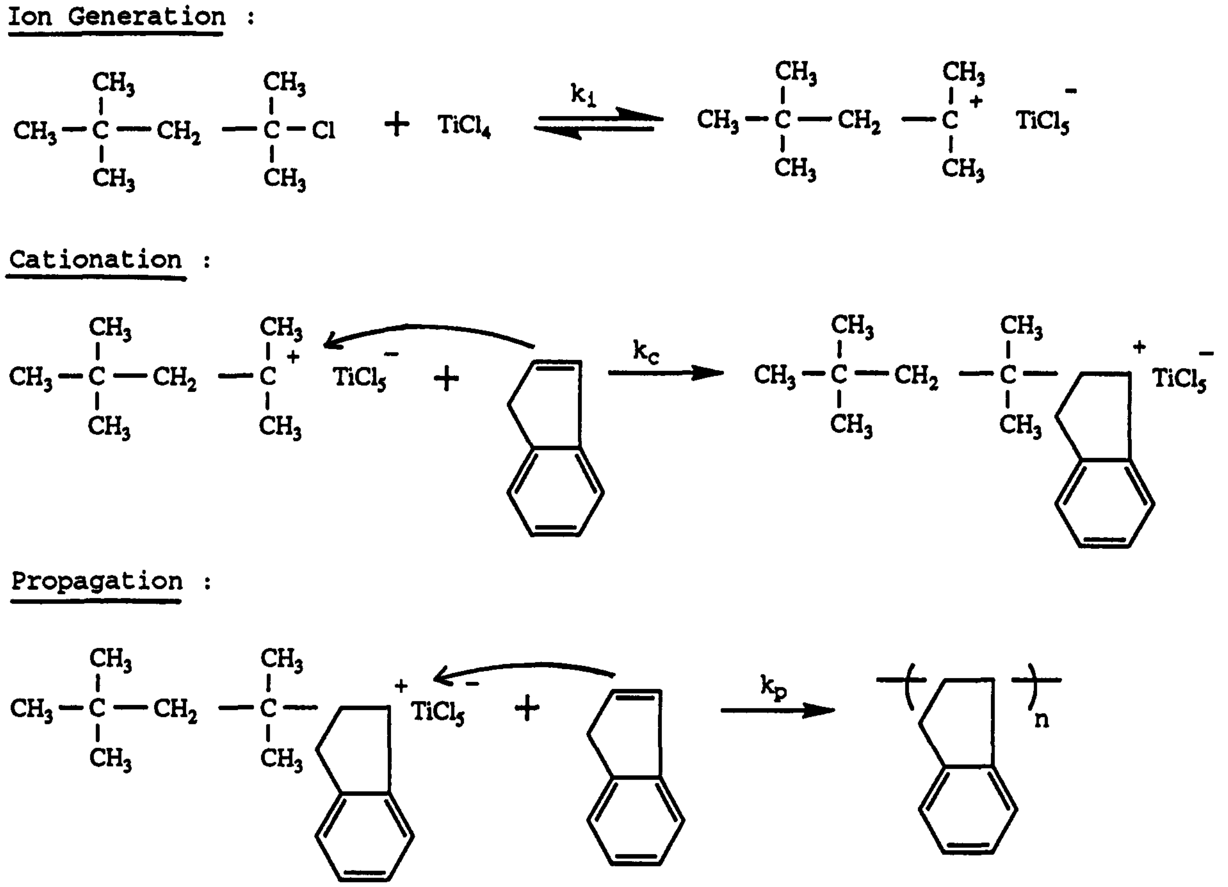
Scheme I
Elementary Steps of Indene Polymerization



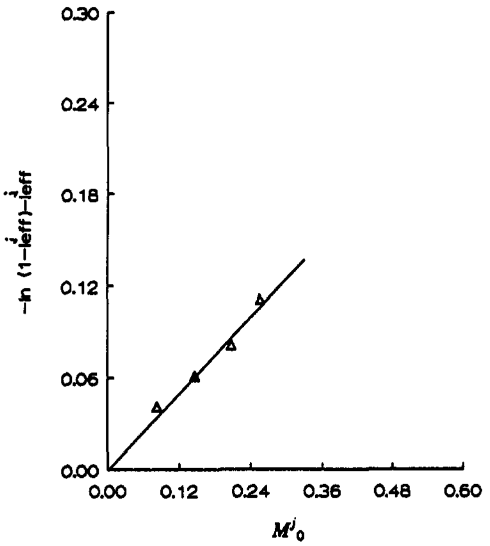


Figure 2. Diagnostic $-\ln(1 - I^j_{eff}) - I^j_{eff}$ versus M^j_0 plot. Experimental conditions are given in Table I.

Results and Discussion

1. Polymerization of Indene by the TMPCl/TiCl$_4$ Initiating System. A series of In polymerizations were carried out in CH$_3$Cl/MCHx (40/60, v/v) solvent mixtures by the conventional AMI technique. The reaction conditions and reagent concentrations were selected on the basis of similar experiments with IB.[3,4] Experimental conditions and results are shown in Table I. The polymerizations were rapid and complete in <6 min. Figure 1 shows the $\bar{M}_n$ versus W_p (weight of the polymer formed) and N (number of polymer molecules obtained (i.e., $(W_p/\bar{M}_n)/I_0$) versus W_p plots.

Table II
Homopolymerization of Indene in the Presence of DMA[a]

no.	W_p (g)	$\bar{M}_n$ expt	$\bar{M}_n$ theo	$\bar{M}_w/\bar{M}_n$	I_{eff} (%)
1	0.2280	8 600	1800	2.49	21
2	0.4534	12 700	3600	2.85	28
3	0.6521	14 350	5200	2.97	36
4	0.8586	20 600	6900	2.96	33
5	1.0580	18 800	8500	3.29	45
6	1.4284	22 550	11400	1.72	51
7[b]	0.1640	24 900		2.00	

[a] Reaction conditions: [TMPCl] = 5.0×10^{-3} M; [TiCl$_4$] = 0.08 M; CH$_3$Cl/MCHx = 40/60 (v/v); [DMA] = 0.01 M; [D*t*BP] = 5×10^{-3} M; V_0 = 25 mL; 6 min; AMI method. DMA = *N,N*-dimethylacetamide; D*t*BP = 2,6-di-*tert*-butylpyridine. Conversions = 100%.
[b] Control experiment (absence of initiator).

Evidently the experimental $\bar{M}_n$'s are much higher than the theoretical values and the moles of polymer formed are much lower than the moles of initiator employed. I_{eff}'s (N/I_0) increased with monomer concentration which is characteristic of the systems in which the rate of initiation is low relative to rate of propagation.[8,9] Scheme I outlines the elementary steps involved in the polymerization.

Figure 2 shows the diagnostic $-\ln(1 - I^j_{eff}) - I^j_{eff}$ versus M^j_0 plot,[8,9] where I^j_{eff} and M^j_0 are the initiation efficiency of the jth reaction and the initial monomer concentration of the jth reaction, respectively. The rectilinear plot starting from the origin corroborates living polymerization with slow initiation[8,9] and suggests cationation to be rate determining. The ratio of rate constants of cationation (k_c) to propagation (k_p) calculated from the slope (k_c/k_p [I_0]) of the line in Figure 2 is 2.14×10^{-3}.

2. Effect of Electron Donors. Recently, the beneficial effects of various electron donors (ED's) and the proton trap (D*t*BP) have been described in detail.[3,10] Thus, a

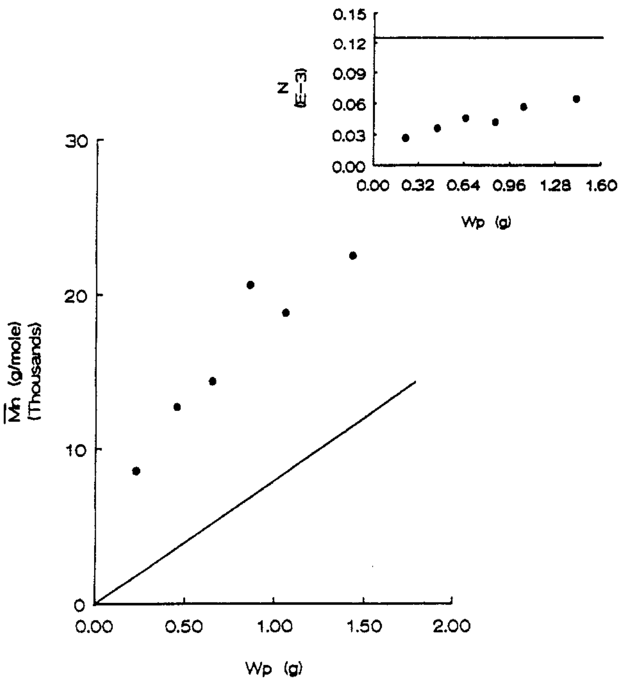


Figure 3. Number-average molecular weights ($\bar{M}_n$) and the number of polymer chains (N) as a function of the weight of PIn formed (W_p). Experimental conditions are given in Table II; solid lines are theoretical (assuming I_{eff} = 100%).

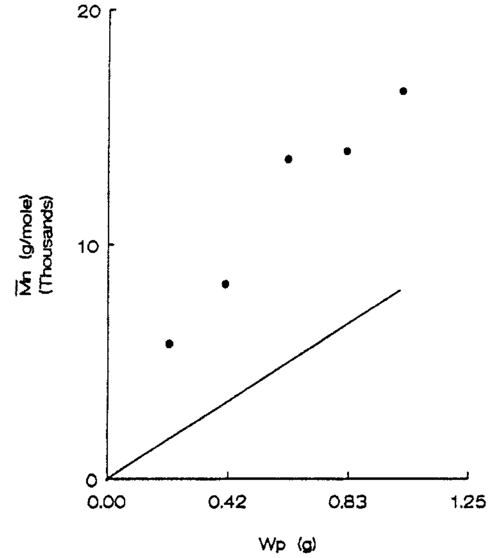


Figure 4. Indene polymerization in the presence of HMPA. [TMPCl] = 5×10^{-3} M; [$TiCl_4$] = 0.08 M; CH_3Cl/MCH_x = 40/60 (v/v); [HMPA] = [D ± BP] = 5×10^{-3} M; V_0 = 30 mL; −80 °C; 5 min; AMI method. The solid line is theoretical (assuming I_{eff} = 100%).

series of experiments was carried out in the presence of DMA (as an ED) and D*t*BP. The concentrations of additives were selected on the basis of similar experiments with IB. Table II and Figure 3 show the results. As shown by the data in Figure 3, the additives apparently do not affect the I_{eff}'s and the overall results. Similar results were also obtained by the use of very strong electron donors such as HMPA (hexamethylformamide) (Figure 4).

The data in Table II have been replotted in Figure 5 according to the diagnostic $-\ln(1 - I^j_{eff}) - I^j_{eff}$ versus M^j_0 plot.[7,8] As exhibited the plot is linear starting from the origin and $k_c/k_p = 2.1 \times 10^{-3}$ from the slope. Surprisingly, the k_c/k_p values are the same in the absence and presence of additives. Evidently the TMPCl/$TiCl_4$/In system is a relatively slowly initiating living polymerization whose k_c/k_p is unaffected by an ED or D*t*BP.

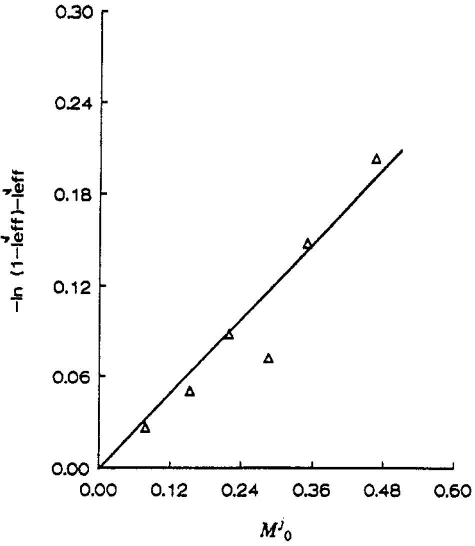


Figure 5. Diagnostic $-\ln(1 - I^j_{eff}) = I^j_{eff}$ versus M^j_0 plot. Experimental conditions are given in Table II.

Table III
Homopolymerization of Indene by the IMA Technique[a]

no.	W_p (g)	$\bar{M}_n$ expt	$\bar{M}_n$ theo	$\bar{M}_w/\bar{M}_n$	I_{eff} (%)
1	0.3255	29 600	2600	2.6	8.7
2	0.6336	47 800	5100	2.7	11.0
3	0.9106	44 200	7300	2.9	16.5
4	1.2139	51 400	9700	2.8	19.0
5	1.4640	52 000	11700	2.6	22.5
6	1.7995	41 600	14400	2.7	34.5
7[b]	0.3351	42 300		2.9	

[a] Reaction conditions: [TMPCl] = 5.0×10^{-3} M; [$TiCl_4$] = 0.08 M; CH_3Cl/MCHx = 40/60 (v/v); [DMA] = 0.1 M; [D*t*BP] = 5.0×10^{-3} M; V_0 = 25 mL; 6 min; IMA technique [6(0.25 mL/5 min)]. Conversions = 100%. [b] Control experiment (absence of initiator).

Table IV
Effect of $TiCl_4$ Concentration of Indene Homopolymerization[a]

no.	W_p (g)	$\bar{M}_n$ expt	$\bar{M}_n$ theo	$\bar{M}_w/\bar{M}_n$	I_{eff} (%)
1	0.6028	9 300	4000	5.3	43
2	0.8041	12 600	5400	5.5	43
3	0.9858	13 000	6600	5.7	51
4	1.1731	15 600	7800	5.7	50

[a] Reaction conditions: [DCE] = 6.0×10^{-3} M; [$TiCl_4$] = 0.18 M; CH_3Cl/MCHx = 40/60 (v/v); [DMA] = 1.8×10^{-2} M; [D*t*BP] = 6.0×10^{-3} M; V_0 = 25 mL; 6 min; AMI method. DCE = 1,4-bis(2-methoxy-2-propyl)benzene. Conversions = 100%.

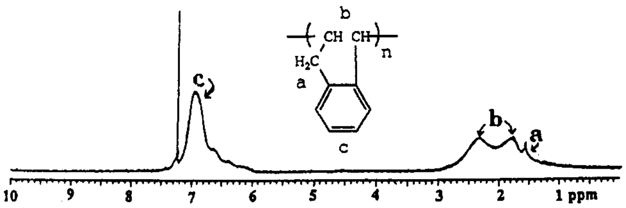


Figure 6. ^1H NMR spectrum of a representative polyindene sample (see text for identification).

An experiment by the IMA technique[6] gave lower I_{eff} values than those obtained by the AMI method. Table III shows the results. The lower I_{eff}'s are probably due to the fact that the PIn^+ cations are more reactive than the residual unreacted TMPCl/$TiCl_4$ initiating complex in the system.

3. Effect of TMPCl/$TiCl_4$ Ratio. An attempt was made to accelerate the rate of initiation relative to that

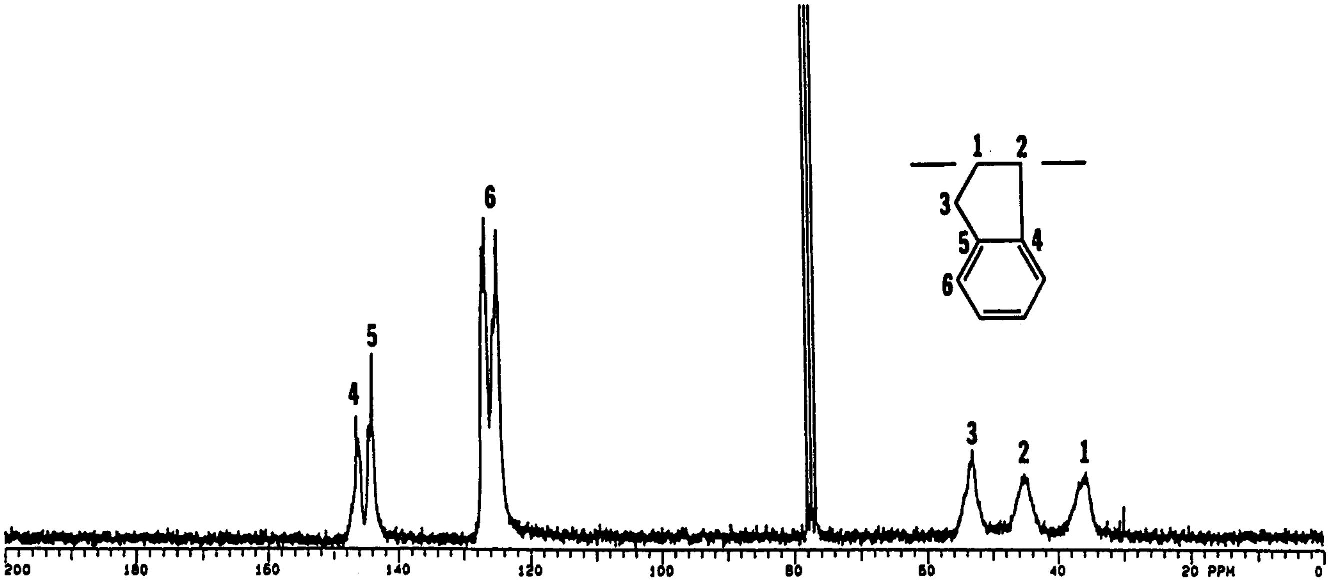


Figure 7. ^{13}C NMR spectrum of a representative polyindene sample (see text for identification).

of propagation by increasing the concentration of $TiCl_4$ from $TMPCl/TiCl_4$ = 1/16 to 1/30. Table IV shows the results. While increased $TiCl_4$ concentration has no effect on I_{eff}, the molecular weight distribution broadened significantly (as expressed by $\bar{M}_w/\bar{M}_n$ data). The latter effect may be due to the increase in moisture initiation[6] introduced by the increased amounts of $TiCl_4$ used.[11]

Characterization. Figures 6 and 7 show the ^1H NMR and ^{13}C NMR spectra, respectively, of a PIn sample together with peak assignments. This sample was prepared by the $TMPCl/TiCl_4/In/CH_3Cl$:MCHx (40/60, v/v)/DMA/D*t*BP/−80 °C system. The absence of olefinic protons in the spectra indicates chain transferless polymerization.

End-Group Characterization. The end-group functionality of a representative PIn sample ($TMPCl/TiCl_4/In/CH_3Cl$:MCHx (40/60, v/v)/TEA/D*t*BP/−80 °C system) was quantitated by a chloride ion selective electrode (CSE).[7] Thus, selective quantitative dehydrochlorination was carried out by sodium biphenyl, followed by aqueous extraction of sodium chloride and Cl^- analysis by CSE. The end functionality of the polymer was 1.15 ± 0.1. The accuracy of this value may be questioned because the $\bar{M}_n$ was determined by GPC using polystyrene calibration.

Thermal Characterization. Surprisingly we found only one source in the scientific literature, in regards to the T_g of PIn. Thus according to Japanese authors the T_g of PIn is 160 °C; however, the molecular weight of the sample has not been mentioned.[12] Figure 8 depicts the DSC trace of one of our representative PIn samples ($\bar{M}_n$ = 27 000) and shows T_g = 204 °C.

Analysis of the Polymerization Mechanism. Scheme I outlines the elementary events of the polymerization of In by the $TMPCl/TiCl_4$ initiating system. The first step is ion pair generation followed by cationation and propagation. Due to the strained nature of the five-membered ring in In, propagation is faster than initiation, which is indicated by the diagnostic slow initiation plots (Figures 1 and 5).

An effort was made to increase the rate of cationation by an aging experiment and thus to increase I_{eff}. In this trial TMPCl and $TiCl_4$ were contacted and aged for 5 min at −80 °C prior to adding this initiating system to the monomer charge. According to the results shown in Table V, aging had only a minor effect on I_{eff} and experimentation was discontinued along this line.

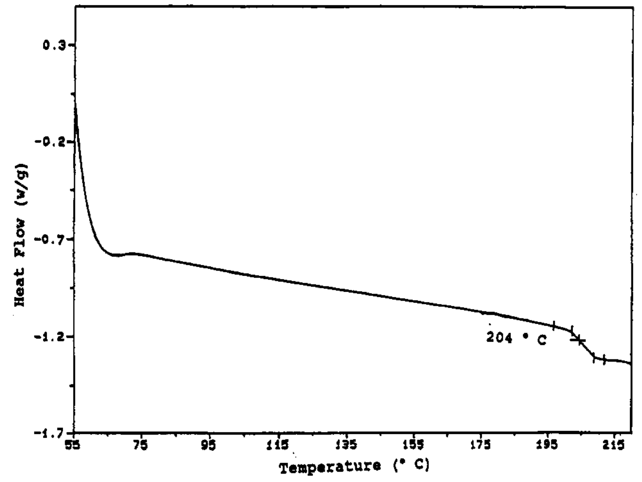


Figure 8. DSC scan of a representative polyindene sample (sample 7 in Table II).

Table V
Effect of Aging of the $TMPCl/TiCl_4$ System on Indene Homopolymerization[a]

no.	W_p (g)	$\bar{M}_n$ expt	$\bar{M}_n$ theo	$\bar{M}_w/\bar{M}_n$	I_{eff} (%)
1	0.2313	2800	1600	2.72	57[b]
2	0.4300	4600	3200	3.21	69[b]

[a] Reaction conditions: [TMPCl] = 5.0×10^{-3} M; [$TiCl_4$] = 0.08 M; CH_3Cl/MCHx = 40/60 (v/v); [DMA] = 0.01 M; [D*t*BP] = 5×10^{-3} M; V_0 = 25 mL; 6 min; AMI method. The initiating complex was aged for 5 min before monomer addition. DMA = *N*,*N*-dimethylacetamide; D*t*BP = 2,6-di-*tert*-butylpyridine. [b] High molecular weight shoulder in the GPC peak.

Cationation is slow, presumably because the approach of the TMP^+ to the double bond in In is sterically inhibited. Thus In is consumed well before all the initiating species are consumed by initiation. This results in low I_{eff}'s and high $\bar{M}_w/\bar{M}_n$ values. Increasing the monomer concentration leads to higher I_{eff} because more new chains can arise before the monomer is consumed.

In many living carbocationic polymerizations the rate of initiation was found to be relatively lower than that of propagation.[6-8] Evidently the polymerization of In initiated by TMPCl also follows this pattern. Similar to the earlier instances, livingness in the In systems can be readily demonstrated by the diagnostic method developed for relatively slow initiation by Zsuga et al.[8]

Table VI
Amount of Water Initiation under Various Experimental Conditions

no.	$[M] \times 10^2$	$\bar{M}_n$	$[N]^a \times 10^4$
1^b	3.68	15 000	2.85
2^c	5.66	24 900	2.63
3^d	11.56	42 300	3.16

[a] Molar concentration of polymer chains. [b] Sample 5 in Table I. [c] Sample 7 in Table II. [d] Sample 7 in Table III.

Polymerizations carried out in the absence of TMPCl also yielded ~100% conversions, most likely because of initiation by adventitious moisture "H_2O". The results of some representative "control" experiments (experiments carried out in the absence of purposely added initiator) shown in Table VI indicate that the number of polymer molecules N is small ($\sim 3 \times 10^{-4}$ M) and that the number virtually remains unchanged even at higher monomer concentrations. Evidently the rate of "H_2O"-induced polymerizations is very high and the polymerizations rapidly consume In. The concentration of the TMPCl initiator was much higher than that of "H_2O" ([TMPCl]/["H_2O"] = 18–20), so the number of PIn chains initiated by "H_2O" was insignificant. Indeed, GPC traces of polymers obtained by the use of TMPCl did not show any evidence for a high molecular weight fraction that would be expected to arise in the presence of significant "H_2O" initiation. These experiments were carried out at low monomer concentrations to facilitate the detection of the high molecular weight "H_2O"-initiated fraction.

Thus, in regards to initiation by "H_2O", we conclude that while most PIn was formed by initiation by TMPCl, some initiation must have also occurred by "H_2O". As indicated by the diagnostic slow initiation plots (cf. Figures 2 and 5), initiation by "H_2O" does not affect the livingness of the PIn^+ chains.

Conclusions

The first living polymerization of In is reported. It can be readily polymerized in a living manner and well-defined PIn's can be produced by living means while such a polymerization would not succeed by anionic techniques, most likely because reactive anions (including propagating anionic species) would preferentially attack the benzylic $-CH_2-$ in the five-membered ring. Aided by the information generated in this research, conditions have been developed for the synthesis of triblock polymers of IB and In by sequential monomer addition. The subsequent paper will discuss the synthesis, characterization, and some physical properties of these novel thermoplastic elastomeric triblocks.

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References and Notes

(1) Puskas, J.; Kaszas, G.; Kennedy, J. P.; Kelen, T. *J. Macromol. Sci., Chem.* **1982–83**, *A18* (9), 1263.

(2) Kaszas, G.; Puskas, J. E.; Chen, C. C.; Kennedy, J. P. *Polym. Bull.* **1988**, *20*, 413.

(3) Kaszas, G.; Puskas, J. E.; Kennedy, J. P.; Hager, W. G. *J. Polym. Sci., Part A: Polym. Chem.* **1991**, *29*, 421.

(4) Kaszas, G.; Gyor, M.; Kennedy, J. P.; Tudos, F. *J. Macromol. Sci., Chem.* **1982–83**, *A18* (9), 1397.

(5) Russell, G. A. *J. Am. Chem. Soc.* **1956**, *78*, 1041.

(6) Faust, R.; Kennedy, J. P. *J. Polym. Sci., Part A: Polym. Chem.* **1987**, *5*, 1847.

(7) Zsuga, M.; Ivan, B.; Kennedy, J. P. *Polym. Bull.* **1989**, *21*, 281.

(8) Zsuga, M.; Kennedy, J. P.; Kelen, T. *J. Macromol. Sci., Chem.* **1989**, *A26* (9), 1305.

(9) Ivan, B.; Zsuga, M.; Gruber, F.; Kennedy, J. P. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1988**, *29*, (2), 33.

(10) Kennedy, J. P.; Ivan, B. *Designed Polymers by Carbocationic Macromolecular Engineering: Theory and Practice*; Hanser: Munich, FRG, 1991.

(11) Kaszas, G.; Puskas, J. E.; Kennedy, J. P. *Macromol. Symp.* **1988**, *13/14*, 473.

(12) Soga, K.; Monoi, T. *Macromolecules* **1989**, *22*, 3823.