experimental results suggest that it is the un-ionized species that participates in the polymerization.

We have proposed a kinetic model using that functional group approach to model the polymerization. In order to include the formation of a multiring polymer, we have used 10 species (A–J), and in order to take care of the unequality of reactive sites, we have used five rate constants. Subsequently, we have accounted for the ionization of melamine and solved the mole balance equations numerically. We have varied the rate constants to fit the experimental data and in this way evaluated all the rate constants of the model. It was found that these rate constants were a function of temperature alone, which is consistent with the basic kinetic theory.

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Registry No. Formaldehyde, 50-00-0; melamine, 108-78-1.

Living Carbocationic Polymerization of *p*-Halostyrenes. 1. Living Poly(*p*-chlorostyrene)†,‡

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ABSTRACT: The living carbocationic polymerization of *p*-chlorostyrene (pClSt) has been achieved by the use of the 2-chloro-2,4,4-trimethylpentane (TMPCl)/$TiCl_4$ initiating system in the presence of dimethylacetamide (DMA) as electron donor and 2,6-di-*tert*-butylpyridine (D*t*BP) as proton trap in CH_3Cl/methylcyclohexane (MCHx) solvent mixtures at −80 °C under conventional laboratory conditions. The living nature of the polymerization was demonstrated by linear $\bar{M}_n$ versus W_p (g of poly(*p*-chlorostyrene) (PpClSt) formed) plots passing through the origin and horizontal N (number of moles of PpClSt formed) versus W_p plots. The $\overline{DP}_n$ obeys [pClSt]/[TMPCl], and the molecular weight distributions (MWD) are narrow, $\bar{M}_w/\bar{M}_n$ = 1.3–1.9. pClSt polymerization by the cumyl methyl ether (CumOMe)/BCl_3 initiating system in CH_3Cl solvent has also been studied. The effects of the nature of the solvent and solvent composition on rates, $\bar{M}_n$s, and MWDs have been investigated. Functionality analysis by chloride-selective electrode, FTIR spectroscopy, and blocking experiments with tetrahydrofuran (THF) demonstrate that end groups of PpClSts are most likely secondary benzylic chlorines and that indanyl end groups are absent. The number-average end functionality ($\bar{F}_n$) was determined to be close to unity.

1. Introduction

Living polymerization is one of the simplest and most effective means to control the molecular weight (MW), MWD, and end functionality of polymers. In view of recent significant advances in living carbocationic polymerization of vinyl ethers[1] and olefins,[2,3] it appeared of interest to investigate that possibility of synthesizing well-defined PpClSt by this new technique.

The cationic polymerization of pClSt has been the subject of previous investigations;[4a] however, studies have not been carried out with respect to end groups, MWs, and MWD control. The polymerization of pClSt by the 1,4-bis(2-chloropropyl)benzene/BCl_3 binifer system has recently been investigated in our laboratories.[4b] While the cationic polymerization of pClSt is somewhat slower than that of other styrene derivatives,[5] we theorized that intramolecular alkylation leading to terminal indanyl structures will not occur on account of the highly deactivated ring. Indanyl structure formation is one of the most difficult to control side reactions in the cationic polymerization of styrenes.[4a] Anionic living polymerization methods cannot be employed for the homo- and copolymerization of pClSt because of the propensity of numerous side reactions.[6] Similarly, free radical

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Table I
Polymerization of p-Chlorostyrene by the CumOMe/BCl_3 Initiating System in Pure CH_3Cl[a]

sample	W_p, g	conv, %	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	$N \times 10^4$, mol	I_{eff}, %
			AMI Technique: 40 min			
1	0.2075	72	4190	1.40	0.49	40
2	0.4364	76	6420	1.61	0.68	55
3	0.6541	75	8500	1.64	0.77	62
4	0.7984	69	10420	1.74	0.77	62
5	0.9478	66	12390	1.79	0.76	62
6[b]	0.0647	11	43550	2.01	0.01	
			IMA Technique: 5 × (0.3 mL of pClSt/15 min)			
7	0.1792	52	8140	1.80	0.22	18
8	0.1830	26	8800	1.84	0.21	17
9	0.2083	20	9820	2.26	0.21	17
10	0.2399	17	11900	2.73	0.20	16
11	0.2637	15	13900	3.13	0.19	15
12[b]	0.0507	7	32000	2.50	0.02	

[a] [CumOMe] = 4.92×10^{-3} M; [BCl_3] = 0.104 M; CH_3Cl = 25 mL; −60 °C. [b] Control ([CumOMe] = 0).

polymerizations are unsuitable for the synthesis of well-defined end-group structures, MWs, and narrow MWDs.

Chlorinated polystyrenes can also be prepared by chlorination of polystyrene. However, the reaction results in randomly substituted ill-defined products. Random substitution occurs mainly in the main chain by radical chlorination and on the aromatic nuclei by ionic processes.[7] The selective chlorination at the para position has not been achieved.[8] Also, both ionic and radical chlorinations are accompanied by rapid molecular weight reduction, indicating severe chain scission.[9] Pyrolysis gas chromatography of ionically chlorinated polystyrenes showed that substitution occurred at both para and ortho ring positions.[7] Teyssie et al.[10] concluded that the first chlorine is preferentially oriented to the para and secondarily to the ortho position and that further substitution yields 3,4-, 2,5-, and, to a lesser extent, 2,4-dichloro-substituted phenyl rings.

This research concerns the synthesis of well-defined narrow-MWD PpClSt by living carbocationic polymerization. PpClSt of controlled MW and narrow MWD would be of interest not only for improved physical–mechanical properties but also for optical, resist, and flame-resistant applications.[11,12]

2. Experimental Section

2.1. Materials. CH_3Cl was dried by passing the gas through a column packed with BaO and condensing it under N_2. MCHx (Lancaster synthesis) was refluxed and distilled from CaH_2 under N_2. $TiCl_4$ (Aldrich) was distilled from P_2O_5 and collected under N_2 on the day of the experiment. D*t*BP and DMA (Aldrich) were used as received. TMPCl was prepared by hydrochlorination of 2,4,4-trimethyl-1-pentene[13] and was vacuum distilled prior to use. The synthesis of pClSt has been described;[14] its purity by GC was 99.9%. The source and purity of BCl_3[15] and the synthesis of CumOMe[3] have been given in detail. THF was distilled from CaH_2 under N_2. Methanol, benzene, and methylene chloride (Fisher) were used as received.

2.2. Polymerization. Polymerizations were carried out in a drybox under a dry nitrogen atmosphere in large (75 mL) test tubes or round-bottom flasks. The moisture level in the charge was monitored by carrying out control experiments (in the absence of initiator). Detailed experiments were carried out by the conventional AMI (all monomer in) and diagnostic IMA (incremental monomer addition) techniques; the details of these techniques have been described.[2] The IMA technique is a sensitive diagnostic procedure for examining the existence of living polymerizations in very fast polymerization systems, i.e., when conventional intermittent sampling to obtain conversion versus time plots is not feasible. Briefly, in the IMA technique a series of test tubes were charged with solvent, TMPCl, D*t*BP, and DMA and thermostated at −80 °C. A solution of $TiCl_4$ was added, the mixture was strongly mixed, and at zero time an appropriate amount of pClSt was added to all the charges. Test tubes were turbomixed and placed in the constant-temperature bath. After a suitable time interval the polymerization was quenched in the first test tube with a few milliliters of chilled methanol while more monomer was added to the rest of the reactors. This procedure was continued until all the charges in the series had been quenched. The solvents were evaporated, the polymers were washed with methanol to remove Ti residues and dried in a vacuum oven, and yields were determined gravimetrically. Subsequently the polymers were purified for analyses by dissolving in CH_2Cl_2, precipitating into CH_3OH, and vacuum drying at room temperature.

The molar concentration of DMA and D*t*BP was usually equal to that of the initiator. Initiator/$TiCl_4$ ratios were 1/16 unless otherwise specified. Further experimental details are given in the tables, figures, and figure captions.

The blocking experiments were carried out at room temperature under a N_2 atmosphere. Thus PpClSt samples were dissolved in THF, and $AgPF_6$ (dissolved in THF) was added. Within seconds the solution turned milky, indicating AgCl precipitation. After suitable time periods (1–5 h) the reaction was quenched by adding few milliliters of CH_3OH, and the solvents were evaporated. The PpClSt-*b*-PTHF product was dissolved in CH_2Cl_2 (good solvent for both block segments) and precipitated into ethanol (good solvent for PTHF and nonsolvent for PpClSt). The polymers were vacuum dried at room temperature and yields were determined.

2.3. Characterization. FTIR and ^1H NMR spectra were recorded by a Beckman FT-2100 and a Varian Gemini 200-MHz instrument, respectively. MWs and MWDs were obtained by a Waters high-pressure GPC assembly (Model 6000 A pump, μStyragel columns of 10^5, 10^4, 10^3, 500, and 100 Å, UV and RI detectors). Elution counts were calibrated by well-fractionated polystyrene standards. THF solutions were used and the flow rate was 1 mL/min. GC analyses were carried out on a Perkin-Elmer instrument (Model 8410). The [Cl^-] was measured by a chloride selective electrode (Orion 9617 U) in combination with an Orion PH-ISE.[16]

3. Results and Discussion

3.1. Polymerization of pClSt Using the CumOMe/BCl_3 Initiating System. It has been reported that the living polymerization of isobutylene is readily induced by the CumOMe/BCl_3 initiating system in CH_3Cl at various temperatures.[3] Thus the polymerization of pClSt has been studied under the same conditions by both the conventional AMI and diagnostic IMA techniques. Polymerizations were rapid and polymer formation could be visually judged by the appearance of cloudiness during stirring. Experimental conditions and results are summarized in Table I.

While $\bar{M}_n$ versus W_p plots (not shown) have suggested some living character (growth of $\bar{M}_n$), the system was judged far from ideal. The reason for the low initiator

Table II
Polymerization of *p*-Chlorostyrene by the TMPCl/$TiCl_4$/CH_3Cl/DMA/D*t*BP System[a]

sample	W_p, g	conv, %	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	$N \times 10^4$, mol	I_{eff}, %
			AMI Technique: 60 min			
1	0.2800	100	3500	1.26	0.80	59
2	0.5700	99	4940	1.32	1.10	82
3	0.8201	96	6130	1.40	1.30	97
4	1.0850	94	7030	1.46	1.50	111
5	1.3920	97	7670	1.51	1.81	135
6[b]	0.2421	40	20570	1.36	0.11	
			IMA Technique: 5 × (0.3 mL of pClSt/20 min)			
7	0.3075	90	5230	2.28	0.59	44
8	0.6360	92	5930	1.73	1.07	79
9	0.9311	90	6720	1.77	1.38	102
10	1.3250	96	7600	1.75	1.74	129
11	1.6250	94	7960	1.55	2.04	152

[a] [TMPCl] = 5.4×10^{-3} M; [$TiCl_4$] = 0.086 M; [DMA] = 4.3×10^{-3} M; [D*t*BP] = 3.6×10^{-3} M; CH_3Cl = 25 mL; −80 °C. [b] Control ([TMPCl] = 0).

Table III
Polymerization of *p*-Chlorostyrene by the TMPCl/$TiCl_4$/CH_3Cl:MCHx (60/40 (v/v))/DMA/D*t*BP System[a]

sample	W_p, g	conv, %	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	$N \times 10^4$, mol	I_{eff}, %
			AMI Technique: 60 min			
1	0.2880	100	3050	1.52	0.94	70
2	0.5770	100	4520	1.53	1.28	95
3	0.8660	100	6650	1.51	1.30	96
4	1.1322	98	7880	1.51	1.44	107
5	1.3824	96	8670	1.52	1.58	117
6[b]	0.0503	9	4700	1.42	0.107	

[a] [TMPCl] = [DMA] = [D*t*BP] = 5.4×10^{-3} M; [$TiCl_4$] = 0.086 M; V_0 = 25 mL; −80 °C. [b] Control ([TMPCl] = 0).

efficiencies ($I_{eff} = N/I_0$, where I_0 is the number of moles of initiator) and relatively broad MWDs may be due to slow cationation

$$C_6H_5\overset{+}{C}(CH_3)_2 + CH_2{=}CH\text{-}pC_6H_4Cl \rightarrow C_6H_5C(CH_3)_2\text{-}CH_2\overset{+}{C}H\text{-}pC_6H_5Cl$$

relative to propagation.

3.2. Polymerization of pClSt by the TMPCl/$TiCl_4$ Initiating System. 3.2.1. Preliminary Experiments. Subsequent to the disappointing results with the CumOMe initiator, extensive preliminary experiments were carried out with the TMPCl/$TiCl_4$ system to find suitable conditions for the living polymerization of pClSt. Initiation (cationation to be precise) was anticipated to be faster with TMPCl than with CumOMe (see equation above). Also TMPCl, an aliphatic tertiary chloride that mimicks the end group of tertiary chlorine capped polyisobutylene (PIB), has been shown to be an efficient initiator in conjunction with $TiCl_4$ for living polymerization.[17] This initiator would model the crossover from the living PIB chain end to pClSt in block polymer synthesis by sequential monomer addition.

In line with experience in these laboratories,[17] DMA was used as the electron donor to help stabilize growing carbocations. The addition of electron donors tends to suppress or eliminate side reactions such as chain transfer, intramolecular alkylation by the growing cations, irreversible chain termination, etc.[17] A similar approach is being used by Higashimura et al.[18] to achieve living polymerization of vinyl ethers.

One disadvantage of the use of $TiCl_4$ over BCl_3 is the extreme moisture sensitivity of the former.[19] Control experiments with $TiCl_4$ consistently produced much larger quantities of polymer than those with BCl_3.[19] To avoid adventitious protic initiation D*t*BP was used as the proton scavenger.

The living polymerizability of pClSt was studied by AMI and IMA experiments initially in CH_3Cl diluent. Table II shows the reagent concentrations and results. Polymerizations were homogeneous and rapid (complete conversions in a few minutes); however, chain transfer was operational, as indicated by the increase in N and I_{eff} values. Nonetheless, the livingness of the system was clearly suggested by the decreasing MWD values with increasing monomer additions by the diagnostic IMA technique.

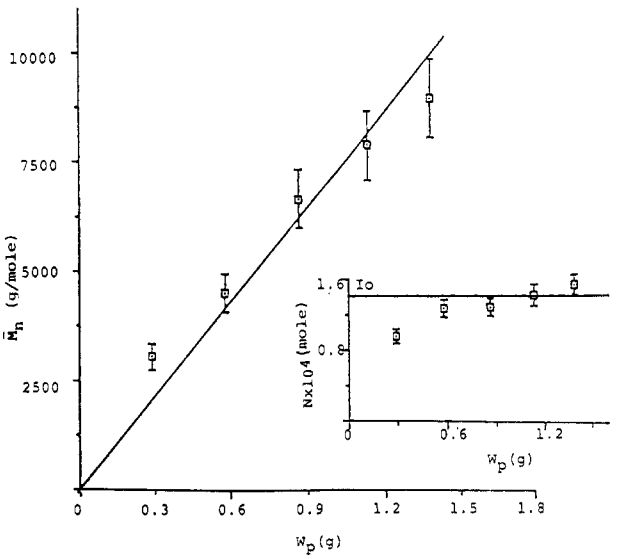

Figure 1. $\bar{M}_n$ and N (inset) versus W_p by the TMPCl/$TiCl_4$/pClSt/CH_3Cl:MCHx (60/40 (v/v)/DMA/D*t*BP/−80 °C system by the AMI technique; conditions as in Table III. Solid lines are theoretical.

According to these results and earlier findings, pure CH_3Cl may be too polar and the carbocations formed were too reactive so that even in the presence of DMA chain transfer could not be avoided. Although there is no direct correlation between the propagation rate constant and the dielectric constant of the solvent,[20] increasing solvent polarity would shift the equilibrium between ion pairs and

Table IV
Living Polymerization of p-Chlorostyrene by the TMPCl/$TiCl_4$/CH_3Cl:MCHx (40/60 (v/v))/DMA/D*t*BP System[a]

sample	W_p, g	conv, %	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	$N \times 10^4$, mol	I_{eff}, %
			AMI Technique: 60 min			
1	0.2980	100	2550	1.37	1.17	87
2	0.5310	92	3900	1.57	1.36	101
3	0.7339	85	5100	1.65	1.44	107
4	1.0113	88	7010	1.77	1.44	107
5	1.2196	85	8300	1.90	1.47	109
6	1.5113	87	10450	1.83	1.45	107
7[b]	0.0239	4	3670		0.06	
			IMA Technique: 6 × (0.25 mL of pClSt/15 min)			
8	0.2317	80	2080	1.37	1.12	82
9	0.4409	76	3200	1.54	1.38	102
10	0.6303	73	4510	1.71	1.40	104
11	0.8724	76	6250	1.77	1.39	103
12	1.1216	78	8010	1.74	1.40	104
13	1.3111	76	9320	1.69	1.41	104
14[b]	0.0317	5	3700	1.84	0.08	

[a] [TMPCl] = [DMA] = [D*t*BP] = 5.4×10^{-3} M; [$TiCl_4$] = 0.086 M; V_0 = 25 mL; −80 °C. [b] Control ([TMPCl] = 0).

Table V
Effect of DMA and D*t*BP on p-Chlorostyrene Polymerization[a]

sample	W_p, g	conv, %	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	$N \times 10^4$, mol	I_{eff}, %
			TMPCl/$TiCl_4$/pClSt/CH_3Cl:MCHx (40/60 (v/v))/D*t*BP/−80 °C			
			AMI Technique: 40 min			
1	0.2680	93	3100	1.78	0.86	64
2	0.5270	91	4510	2.00	1.17	87
3	0.8010	92	6190	2.10	1.29	96
4	1.0205	88	7560	2.56	1.35	100
5	1.2147	84	8770	2.70	1.38	103
6[b]	0.0507	9	6070	2.66	0.08	
			TMPCl/$TiCl_4$/pClSt/CH_3Cl:MCHx (40/60 (v/v))/DMA/−80 °C			
			AMI Technique: 40 min			
7	0.2580	90	2600	1.59	0.99	76
8	0.5212	90	4220	1.75	1.23	92
9	0.7909	91	5850	1.86	1.35	100
10	1.0798	93	8170	1.93	1.32	98
11	1.2506	87	8980	2.10	1.39	103
12[b]	0.0474	8	6270	2.35	0.07	

[a] [TMPCl] = [DMA] = [D*t*BP] = 5.4×10^{-3} M; [$TiCl_4$] = 0.086 M; V_0 = 25 mL. [b] Control ([TMPCl] = 0).

free ions toward ion separation[21] and thus facilitate chain transfer.

To reduce solvent polarity and thus to eliminate chain transfer, we have carried out pClSt polymerizations in the mixed polar/nonpolar solvent system CH_3Cl/MCHx (60/40 (v/v)). Results are summarized in Table III. Polymerizations were homogeneous and 100% conversions were obtained in a few minutes. The MWDs were ~1.5 in all experiments; however, N and I_{eff} increased gradually, indicating slow chain transfer. Figure 1 shows the $\bar{M}_n$ versus W_p and N versus W_p plots (inset). The error bars in this figure (and all the subsequent figures) were calculated by assuming a ±10% error in GPC ($\bar{M}_n$) measurements. It is evident that a small measure of chain transfer still persists, as indicated by the small deviation of the $\bar{M}_n$ versus W_p plot and N versus W_p plot from the theoretical line. Nonetheless, the reducing of the polarity of the medium greatly helped approaching living polymerization conditions.

3.2.2. Demonstration of Living pClSt Polymerization. In view of the above preliminary experiments, the polymerization of pClSt by the TMPCl/$TiCl_4$ initiating system in the even less polar 40/60 (v/v) CH_3Cl/MCH_x solvent mixture at −80 °C was further studied. Table IV shows experimental conditions and results. Polymerizations became first cloudy and then heterogeneous (i.e., precipitation became visible) as the molecular weight approached $\bar{M}_n \cong$ 5000–6000. By the use of 45/55 (v/v) CH_3Cl/MCHx the first signs of heterogeneity were delayed to $\bar{M}_n \sim$ 10 000. At higher polarity (i.e., 60/40 (v/v) CH_3Cl/MCHx, although the system remained homogeneous throughout the course of the polymerization, the danger of chain transfer existed (see also Table III). On account of the rather large proportion of the nonpolar component in this solvent mixture, the rates of polymerizations were low. The I_{eff}s were nearly 100% in all the experiments. The MWDs are narrow, i.e., 1.3–1.9; the broadening of the $\bar{M}_w/\bar{M}_n$ values may be due to the heterogeneous nature (insufficient stirring etc.) of the polymerization.

Figures 2 and 3 show the $\bar{M}_n$ versus W_p and N versus W_p plots (insets) for the AMI and IMA experiments, respectively. According to the linear $\bar{M}_n$ versus W_p plots passing through the origin and the horizontal N versus W_p plots, the polymerizations are living. The experimental points lie close to the theoretical lines in both the $\bar{M}_n$ versus W_p and N versus W_p plots, indicating that the number of PpClSt molecules formed are close to the number of the initiator molecules (I_0) used, signifying the virtual absence of chain transfer. Figure 4 shows the GPC traces of polymers obtained from the IMA experiment.

Next we studied the effect of electron donors on polymerization details. In particular, we were interested in the effect of DMA and D*t*BP on the living polymerization of pClSt. Table V shows the results of two series of experiments, one with DMA (without D*t*BP) and

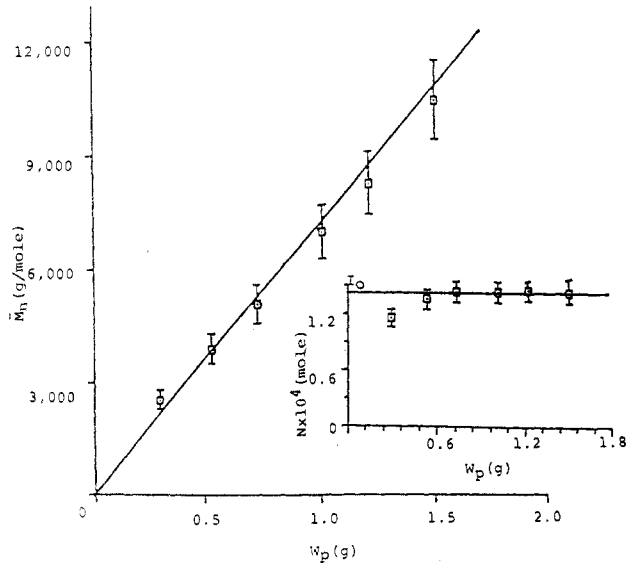

Figure 2. $\bar{M}_n$ and N (inset) versus W_p by the TMPCl/$TiCl_4$/pClSt/CH_3Cl:MCHx (40/60 (v/v))/DMA/D*t*BP/−80 °C system by the AMI technique; conditions as in Table IV. Solid lines are theoretical.

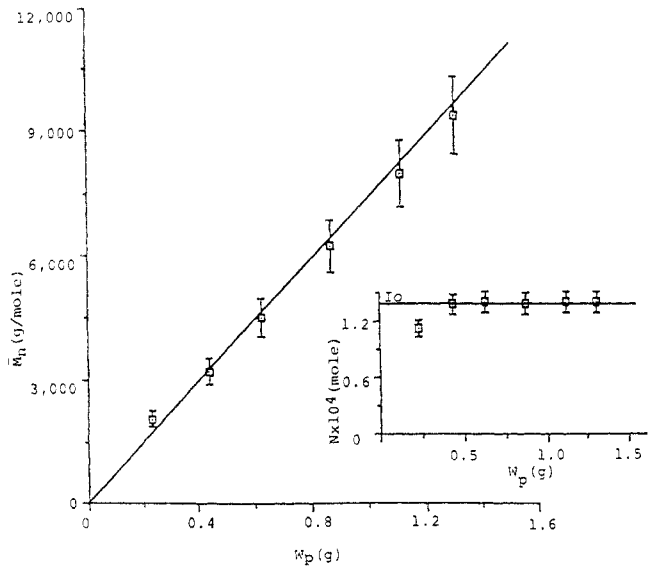

Figure 3. $\bar{M}_n$ and N (inset) versus W_p by the TMPCl/$TiCl_4$/pClSt/CH_3Cl:MCHx (40/60 (v/v))/DMA/D*t*BP/−80 °C system by the IMA technique; conditions as in Table IV. Solid lines are theoretical.

the other with D*t*BP (without DMA). Polymerizations became heterogeneous as the molecular weight was increased and the rates of polymerizations were low. Figure 5 shows the $\bar{M}_n$ versus W_p and N versus W_p plots (inset). In both cases living polymerizations prevailed. According to these results D*t*BP, in addition to being a proton scavenger, may also function as an electron donor; i.e., it stabilizes the carbocations. Similarly, the DMA also exerts a dual cation stabilizing *and* proton scavenging function. However, in terms of MWD, N, and I_{eff} data, better results were obtained when both DMA and D*t*BP were present.

In the absence of both DMA and D*t*BP under the same conditions, the product exhibits broad and bimodal ($\bar{M}_w/\bar{M}_n$ = 4.34) MWD; i.e., the systems are nonliving.

Experiments were also carried out at −40 °C with the TMPCl/$TiCl_4$ initiating system in CH_3Cl/MCHx (40/60 (v/v)). Polymerization time was 70 min. According to the findings (not shown) chain transfer occurs at this temperature as evidenced by relatively high I_{eff} values (i.e., I_{eff} = 114% at 57% conversion).

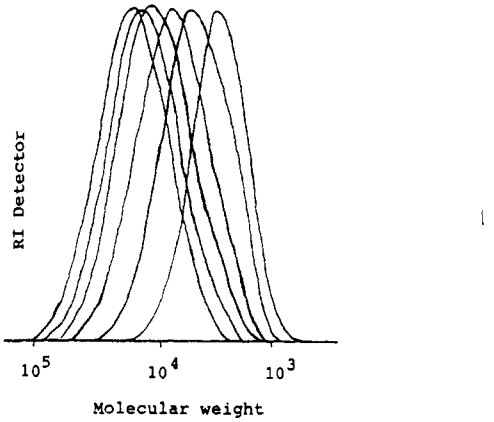

Figure 4. GPC traces of PpClSts obtained by the TMPCl/$TiCl_4$/pClSt/CH_3Cl:MCHx (40/60 (v/v))/DMA/D*t*BP/−80 °C system; IMA technique; conditions as in Table IV.

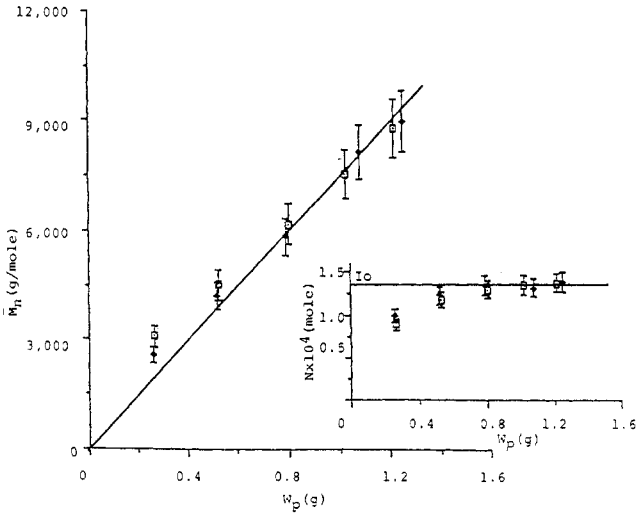

Figure 5. $\bar{M}_n$ and N (inset) versus W_p plots to show the effect of DMA and D*t*BP on pClSt polymerization. AMI technique: (□) without DMA; (♦) without D*t*BP; conditions as in Table V. Solid lines are theoretical.

3.3. End-Group Characterization. A very sensitive microanalytical method has recently been developed for the determination of small amounts of active chlorine end groups (e.g., tertiary aliphatic, secondary benzylic) in the presence of large amounts of less reactive chlorines.[16] The method involves selective quantitative dehydrochlorination of PpClSt by *t*-BuOK, aqueous extraction of the KCl, and [Cl^-] determination by a chloride selective electrode. Two representative PpClSt samples prepared under the general conditions shown in Table IV with the AMI technique and purified by three reprecipitations from benzene into methanol ($\bar{M}_n$ = 5300 and 6500) gave $\bar{F}_n$ (number-average end functionality) = 1.00 and 1.06, respectively. These values are reliable to ±0.1 (i.e., ~10% error, mainly due to the GPC method of MW determination). Thus by the use of this method we could determine selectively the concentration of the terminal secondary benzylic chlorines (~$CH_2CH(C_6H_4Cl)Cl$) in the presence of a large number of less reactive para chlorines. These close to theoretical $\bar{F}_n$ values also suggest the absence of indanyl end structures.

FTIR spectroscopy provided further useful information in regard to end-group structure. Figure 6 shows the characteristic region of the FTIR spectrum of a select PpClSt sample ($\bar{M}_n$ = 8900). Absorption bands are absent between 830 and 920 cm^{-1}, indicating the absence of ring C–H deformation vibrations characteristic of indanyl

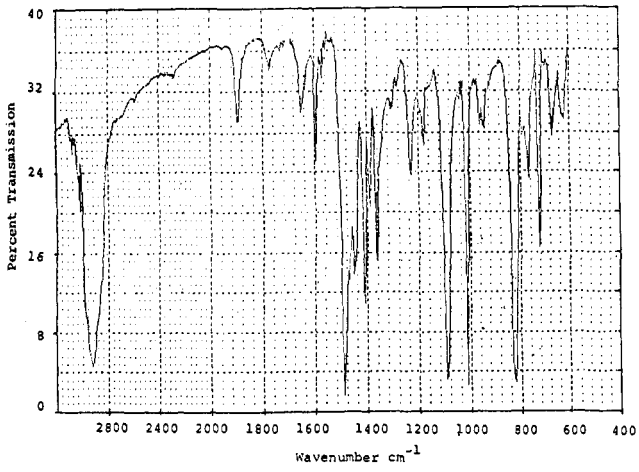

Figure 6. FTIR spectrum of a PpClSt sample ($\bar{M}_n$ = 8900) prepared by the TMPCl/$TiCl_4$/pClSt/CH_3Cl:MCHx (40/60 (v/v))/DMA/D*t*BP/−80 °C system; AMI technique.

structures.[22,23] Thus within the accuracy of this method indanyl structures are absent.

Neither ^1H NMR (200 MHz) nor ^{13}C NMR spectroscopy gave useful information in regard to indanyl ring structure analysis because of severe resonance overlap. Our findings are in good agreement with those reported by Kiji et al.,[24] who investigated the cationic oligomerization of pClSt and did not find any indanyl rings.

Compelling qualitative proof for the presence of secondary benzylic chlorine end groups also comes from blocking experiments. Thus THF was blocked from the secondary benzylic chlorine end of PpClSt. The ^1H NMR spectrum of the product obtained after selective precipitation (see Experimental Section) indicated the presence of both PpClSt and PTHF sequences. Blocking efficiency (moles of PTHF/mole of secondary benzylic Cl end groups) calculated by ^1H NMR spectroscopy was ~100%. The blocking of THF from secondary benzylic chlorine end groups will be the subject of a future publication.

4. Conclusion

We have demonstrated the living carbocationic polymerization of pClSt by the use of the TMPCl/$TiCl_4$ initiating system in the presence of DMA and D*t*BP in the CH_3Cl/MCHx (40/60 (v/v)) solvent system at −80 °C. End-group characterization including chloride selective electrode, blocking experiments with THF, and FTIR spectroscopy did not show evidence for indanyl structures and suggests one secondary benzylic chlorine per end group ($\bar{F}_n$ = 1.0 ± 0.1).

Exploitation of the above information for the synthesis of various block polymers is underway. The TMPCl initiator is a model of the living polyisobutylene chain end, and in this sense pClSt homopolymerizations are model experiments for blocking pClSt from living polyisobutylene cations by sequential monomer addition. Forthcoming papers of this series will discuss the synthesis, characterization, and some physical properties of novel diblock, triblock, and radial block polymers of isobutylene and pClSt. Experiments in progress are directed toward the extension of the scope of these polymerizations to *p*-fluoro- and *p*-bromostyrenes. Detailed studies on the stereoregularity of poly(*p*-halostyrenes) by ^1H and ^{13}C NMR spectroscopy will also be part of this series.

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