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LIVING CARBOCATIONIC POLYMERIZATION. XXXIX. ISOBUTYLENE POLYMERIZATION IN THE PRESENCE OF PYRIDINE AND VARIOUS OTHER ELECTRON DONORS

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ABSTRACT

Aspects of the living polymerization of isobutylene (IB) initiated by the 2-chloro-2,4,4-trimethylpentane (TMPCl)/TiCl₄ combination have been investigated in the presence and absence of di-*tert*-butylpyridine (DtBP) and various electron donors (ED), such as pyridine, tri-*n*-butylamine, di-*n*-butylamine, *N,N*-dimethylacetamide, *N,N*-dimethylformamide, urea, nitromethane, acetonitrile, acetone, acetyl chloride, tetrahydrofuran, tri-*n*-butyl phosphine, triethylphosphite, dimethyl sulfide, and dimethylsulfoxide. All these EDs, commonly regarded as “poisons” of cationic polymerizations, exert, in fact, beneficial effects; for example, they cause the narrowing of molecular weight distributions (MWD). The active agents are TiCl₄·ED complexes which in some systems may be partially insoluble and precipitate from the charges. A detailed series of experiments with the TMPCl/TiCl₄/IB/pyridine system demonstrates the living nature of these polymerizations.

INTRODUCTION

In the course of our ongoing investigations on the use of EDs for the control of living carbocationic polymerization (LC⁺Pzn) of IB [1–3], we

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have screened a large number of EDs as to their effect on various product characteristics, in particular MWD. We have discovered that numerous strong EDs, including pyridine and other amines, conventionally regarded as powerful poisons of cationic polymerizations, readily mediate the LC^+Pzn of IB and produce narrow MWD polyisobutylene (PIB) under mild laboratory conditions.

EXPERIMENTAL

Materials

The synthesis of $TMPCl$ and the sources and purification of IB, CH_3Cl , *n*-hexane, and $TiCl_4$ have been described [4-6]. Pyridine, tri-*n*-butylamine, and di-*n*-butylamine were distilled over KOH. Acetyl chloride, nitromethane, and triethyl phosphite were distilled over $MgSO_4$. Acetonitrile was distilled over P_2O_5 . Acetone was distilled over K_2CO_3 . *N,N*-Dimethylformamide (DMF) was distilled over CaH_2 . Tetrahydrofuran (THF) was distilled over Na. Methanol (Fisher), dimethylsulfoxide (DMSO, Aldrich), *N,N*-dimethylacetamide (DMA, Aldrich), 2,6-di-*tert*-butylpyridine (*DtBP*, Aldrich, 97%), tri-*n*-butylphosphine (Aldrich), dimethyl sulfide (Aldrich) and urea (Aldrich) were used as received.

Procedures

Polymerizations were carried out in a dry box under a blanket of dry nitrogen in large test tubes (75 mL). The details of polymerization and characterization methods have been described [5-7]. The compositions of individual systems have been developed in earlier investigations and were found to be conducive to LC^+Pzn . Specific conditions, including concentrations, etc., are given in the text and in the captions to the tables and the figures.

RESULTS AND DISCUSSION

1. Orienting Experiments

In this research we have exclusively used the $TMPCl/TiCl_4$ initiating system. $TiCl_4$ is notorious for uncontrolled alkene polymerizations by adventitious coinication in the presence of putative protic impurities

TABLE 1. The Effect of *Dt*BP and DMSO on IB Polymerization (control experiments in the absence of TMPCl)^a

Run	<i>Dt</i> BP, \bar{M}	DMSO, \bar{M}	Conversion, %	\bar{M}_n	\bar{M}_w/\bar{M}_n
1	—	—	89	59,100	2.14
2	0.004	—	1	23,300	2.66
3	—	0.012	8	20,600	1.39
4	0.004	0.012	1	11,700	2.34
5	0.008	0.012	1	12,200	2.06

^a[IB] = 3.32 *M*, [TiCl₄] = 0.051 *M*, CH₃Cl/*n*-hexane = 70/30, total volume = 35 mL, -40°C, 30 min.

(moisture). To overcome the latter problem, we have employed the proton trap *Dt*BP. Table 1 shows the effects of *Dt*BP and DMSO on the conversion, \bar{M}_n , and MWD of PIB in "control" experiments, i.e., polymerizations induced most likely by moisture in the absence of TMPCl. As expected, in the absence of *Dt*BP and DMSO (Run 1), uncontrolled polymerization occurs; the \bar{M}_n very high, indicating a "runaway" polymerization leading to the anticipated broad MWD. Similarly, as expected, in the presence of the proton trap insignificant conversions occurred (Runs 2, 4, and 5). Interestingly, in the absence of *Dt*BP but the presence of DMSO, a measurable conversion and significantly narrower MWD were obtained (Run 3).

The data collected in Tables 2-4 show the effect of the proton trap and DMSO (Tables 2 and 3) and the proton trap and DMA (Table 4) on

TABLE 2. The Effect of *Dt*BP and DMSO on IB Polymerization^a

Run	IB, <i>M</i>	TMPCl, <i>M</i>	Conversion, %	\bar{M}_n	\bar{M}_w/\bar{M}_n	<i>I</i> _{eff} , %
1	3.32	0.014	70	11,700	1.17	80
2	1.16	0.014	60	3,850	1.11	73
3	1.16	0.028	86	2,700	1.15	75

^a[TiCl₄] = 0.051 *M*, [*Dt*BP] = 0.008 *M*, [DMSO] = 0.012 *M*, CH₃Cl/*n*-hexane = 70/30, total volume = 35 mL, -40°C, 30 min.

TABLE 3. The Effect of *Dt*BP and DMSO on IB Polymerization^a

Run	<i>Dt</i> BP, <i>M</i>	DMSO, <i>M</i>	Conversion, %	\bar{M}_n	\bar{M}_w/\bar{M}_n	I_{eff} , %
1	—	—	~100	4150	11.64 ^b	61
2	0.002	—	~100	3690	1.13	69
3	0.004	—	~100	3660	1.14	69
4	—	0.006	~100	3730	1.15	68
5	—	0.012	~100	3430	1.15	73
6	0.001	0.003	~100	3670	1.14	71
7	0.002	0.006	~100	3560	1.13	73
8	0.004	0.012	~100	3560	1.11	71

^a[IB] = 1.16 *M*, [TiCl₄] = 0.051 *M*, [TMPCl] = 0.028 *M*, CH₃Cl/*n*-hexane = 55/45, total volume = 34.5 mL, -40°C, 1 h.

^bBimodal MWD.

IB polymerization under various conditions. In all these experiments the introduction sequence of the chemicals was: ① ED, ② solvent, ③ TMPCl, ④ TiCl₄, and finally ⑤ IB. In every reactor (except, of course, in the "control," Run 1, Table 3) a fine white precipitate, presumably TiCl₄·ED complexes, formed before the IB was added to the charge. The data in the tables demonstrate the beneficial effects on conversion, MWD, and I_{eff} of either the proton trap and/or these EDs, and the

TABLE 4. The Effect of *Dt*BP and DMA on IB Polymerization^a

Run	[<i>Dt</i> BP], <i>M</i>	[DMA], <i>M</i>	Temperature, °C	Conversion, %	\bar{M}_n	\bar{M}_w/\bar{M}_n	I_{eff} , %
1	0.005	—	-40	~100	4120	1.25	75
2	—	0.005	-40	~100	3900	1.32	77
3	0.005	0.005	-40	~100	3780	1.20	80
4	0.005	—	-20	98	3550	1.36	81
5	—	0.005	-20	99	3480	1.41	84
6	0.005	0.005	-20	99	3590	1.49	81

^a[IB] = 1.21 *M*, [TiCl₄] = 0.097 *M*, [TMPCl] = 0.024 *M*, CH₃Cl/*n*-hexane = 70/30, total volume = 34.5 mL, 30 min.

superior control achieved in the presence of even small amounts of both of these additives. We are reluctant at this time to discuss further the significance or influence of precipitate formation in these polymerizations. Research is in progress and much more information is needed before this phenomenon can be analyzed. The significant fact, however, remains that LC^+Pzn can be readily demonstrated in a variety of systems and under a variety of conditions in which precipitate formation prior to polymerization has been observed. The narrow MWDs ($\overline{M}_w/\overline{M}_n \approx 1.1$) clearly indicate LC^+Pzn s. The cause for the less than 100% initiator efficiency ($I_{eff} = 70\text{--}80\%$) is obscure; perhaps the precipitate removes a fraction of the $TMPCl$. In contrast to the above experiments, 93–97% I_{eff} s were obtained by using the following reagent introduction sequences: ① ED ② solvent ③ $TiCl_4$ ④ $TMPCl$ ⑤ IB (see, for example, Fig. 2); and ① ED ② solvent ③ $TMPCl$ ④ IB ⑤ $TiCl_4$ or ① $TMPCl$ ② solvent ③ $TiCl_4$ ④ ED ⑤ IB.

2. LC^+Pzn in the Presence of Various EDs

It has been theorized that the species that mediate the LC^+Pzn of IB are $TiCl_4 \cdot ED$ complexes formed upon contacting EDs with $TiCl_4$, and not the “free” EDs [7, 9]. Thus, in line with the earlier observations and the above experiments, a series of screening experiments has been carried out in which various $TiCl_4 \cdot ED$ complexes were prepared and their effect on IB polymerization under similar conditions were determined. (Our symbolism $TiCl_4 \cdot ED$ should not be misconstrued to signify exclusively stoichiometric complexes.)

Table 5 summarizes the data obtained with 14 common EDs, including esters, ethers, carbonyl compounds, amines, amides, cyanides, nitro compounds, etc.; nucleophiles known to form complexes with $TiCl_4$ [8], and Fig. 1 shows some typical GPC traces of the products in Table 5. In several instances, precipitation was observed prior to polymerization, presumably caused by the low solubility of some $TiCl_4 \cdot ED$ complexes (see Footnote b in Table 5). PIB is readily soluble in the charges under these conditions. The data indicate a general beneficial effect exerted by the EDs or rather by the $TiCl_4 \cdot ED$ complexes. Almost invariably the $TiCl_4 \cdot ED$ complexes cause a narrowing of the MWD, suggesting a trend toward LC^+Pzn . However, this effect is independent of the solubility of these complexes. For example, the \overline{M}_n and MWDs of the PIBs formed in the presence of $n\text{-Bu}_3N$ and DMA (Runs 4 and 8) were almost identical although the former system was soluble while the latter gave precipitate

TABLE 5. The Effect of various EDs on IB Polymerization^a

Run	ED	Concentration, <i>M</i>	Conversion, %	\overline{M}_n	$\overline{M}_w/\overline{M}_n$	I_{eff} , %
1	—	—	99	3930	3.87	75
2	Pyridine	0.005	~100 ^b	4410	1.48	68
3	Pyridine	0.050	~100 ^b	4240	1.25	71
4	<i>n</i> -Bu ₃ N	0.005	98	4190	1.38	69
5	<i>n</i> -Bu ₃ N	0.050	31	1880	1.29	49
6	<i>n</i> -Bu ₂ NH	0.005	~100	4280	1.51	70
7	<i>n</i> -Bu ₂ NH	0.050	~100	4220	1.40	72
8	DMA	0.005	~100 ^b	3150	1.31	96
9	DMA	0.050	~100 ^b	3080	1.37	97
10	DMF	0.005	92 ^b	3560	1.38	77
11	DMF	0.050	~100 ^b	3600	1.21	83
12	NH ₂ CONH ₂	0.005	~100	3340	2.32	91
13	NH ₂ CONH ₂	0.050	~100	3360	2.22	90
14	CH ₃ NO ₂	0.005	~100	3660	3.28	83
15	CH ₃ NO ₂	0.050	~100 ^b	3270	1.65	90
16	CH ₃ CN	0.005	98	4030	1.35	75
17	CH ₃ CN	0.050	~100 ^b	3830	1.40	78
18	CH ₃ COCH ₃	0.005	98	3860	1.84	75
19	CH ₃ COCH ₃	0.050	~100 ^b	3740	1.47	79
20	CH ₃ COCl	0.005	95	3310	2.18	85
21	CH ₃ COCl	0.050	91	2680	1.38	100
22	THF	0.004	~100	4230	1.92	71
23	THF	0.044	~100 ^b	3770	2.12	80
24	<i>n</i> -Bu ₃ P	0.005	~100	4420	1.49	68
25	<i>n</i> -Bu ₃ P	0.050	~100	4110	1.32	73
26	(EtO) ₃ P	0.005	93	4290	1.47	64
27	(EtO) ₃ P	0.050	~1	2000	1.38	—
28	(CH ₃) ₂ S	0.005	~100	3900	1.46	77
29	(CH ₃) ₂ S	0.050	~2	4420	1.87	—

^a[IB] = 1.21 *M*, [TiCl₄] = 0.097 *M*, [TMPCl] = 0.024 *M*, CH₃Cl/*n*-hexane = 70/30, total volume = 34.5 mL, -40°C, 30 min.

^bPrecipitate formation before polymerization.

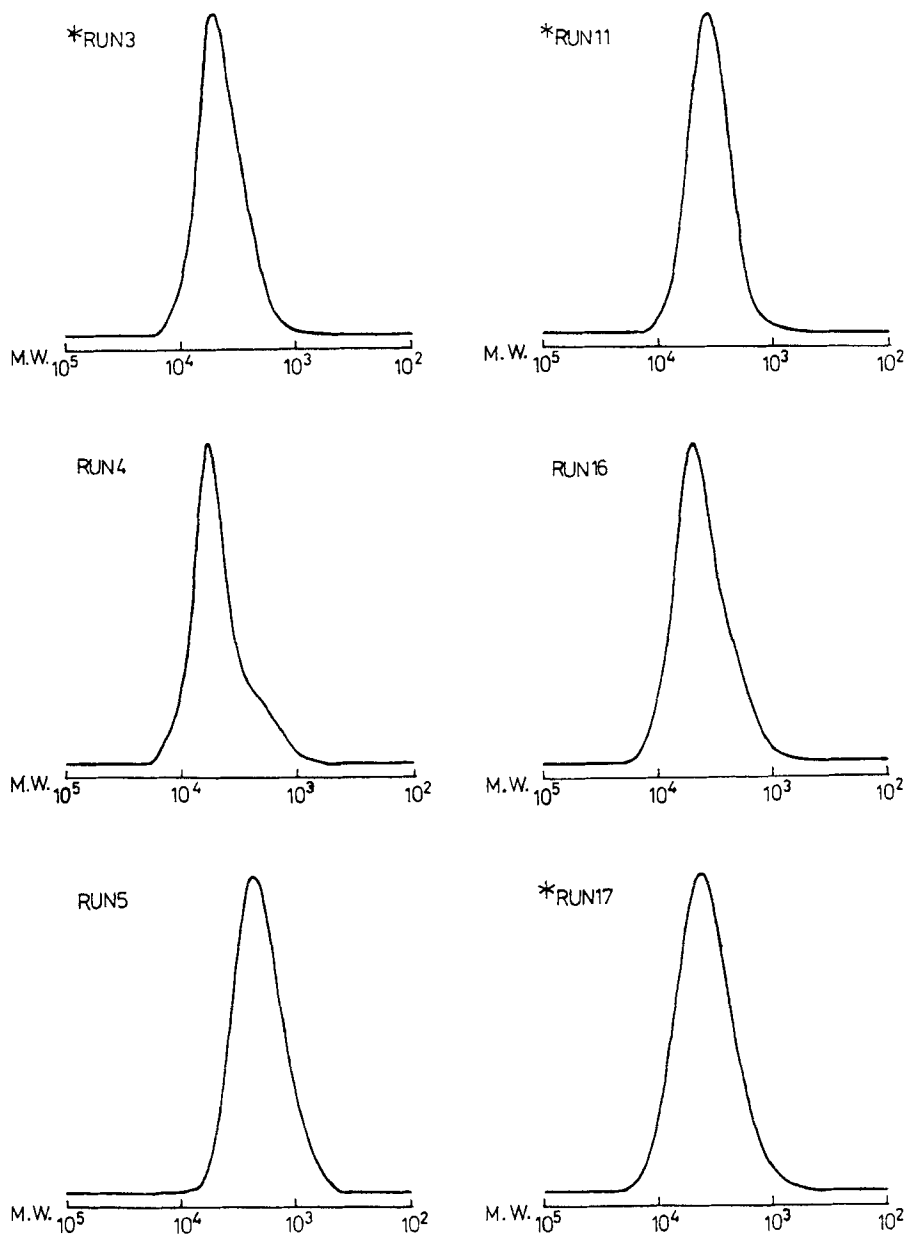


FIG. 1. Representative GPC (IR) traces of PIBs synthesized in the presence of various EDs. Run number refers to the data in Table 5. Asterisks indicate precipitate formation before polymerization.

TABLE 6. The Effect of ED Concentration on IB Polymerization^a

Run	ED	ED, <i>M</i>	ED/ TiCl ₄ , <i>M/M</i>	Conversion, %	\overline{M}_n	$\overline{M}_w/\overline{M}_n$	<i>I</i> _{eff} , %
1	Pyridine	0.005	1/20	~100	4530	1.18	67
2	Pyridine	0.024	1/4	~100	4400	1.38	68
3	Pyridine	0.048	1/2	~100	4050	1.35	73
4	Pyridine	0.097	1/1	99	3970	1.38	74
5	Pyridine	0.194	2/1	0	—	—	—
6	Pyridine	0.291	3/1	0	—	—	—
7	Pyridine	0.388	4/1	0	—	—	—
8	DMF	0.005	1/20	~100	3800	1.35	79
9	DMF	0.050	1/2	~100	3770	1.60	80
10	DMF	0.073	1/1.5	92	3270	1.15	83
11	DMF	0.097	1/1	24	1020	1.32	71
12	DMF	0.145	1.5/1	0	—	—	—
13	DMF	0.194	2/1	0	—	—	—
14	DMF	0.291	3/1	0	—	—	—

^a[IB] = 1.21 *M*, [TiCl₄] = 0.097 *M*, [TMPCl] = 0.024 *M*, CH₃Cl/*n*-hexane = 70/30, total volume = 34.5 mL, -40°C, 30 min. Chemicals introduction sequence: ① ED ② Solvents ③ TMPCl ④ TiCl₄ ⑤ IB.

upon DMA addition. Or, the \overline{M}_n s, MWDs, and *I*_{eff}s are independent of CH₃CN concentration (as long as [CH₃CN]/[TiCl₄] < 1) and the presence-or-absence of precipitate (Runs 16 and 17). Evidently a small quantity of dissolved TiCl₄·ED complex suffices to mediate LC⁺Pzn.

The effect of aliphatic and heterocyclic amines (Runs 2-7) are of particular interest since these compounds are commonly viewed to be strong poisons of cationic polymerizations. We have selected pyridine and DMF for further studies. Table 6 shows representative data in which the effect of the relative concentration of these additives (i.e., ED/TiCl₄ ratio) on polymerization details was surveyed. Evidently, polymerizations occurred only when the ED/TiCl₄ ratio was less than unity. As soon as this ratio exceeded 1.0, polymerizations were absent. According to these data, the 1:1 ED/TiCl₄ complex (at least with pyridine and DMF) is the species that mediates LC⁺Pzn. Very similar observations have also been made by Faust et al. [7, 9].

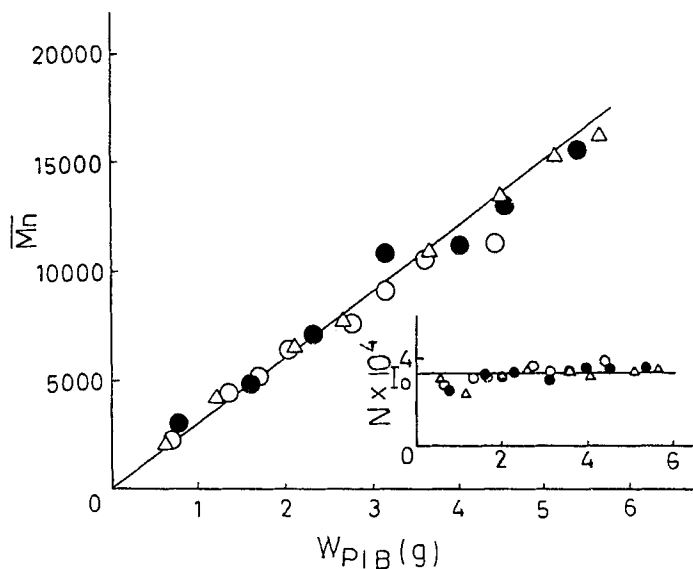


FIG. 2. \bar{M}_n and N , the number of PIB moles (inset) versus W_{PIB} weight of PIB formed in experiments with the TMPCl/TiCl₄/pyridine/IB/−40 and −80°C systems. IMA technique, −80°C (●), IMA technique, −40°C (○), AMI technique, −40°C (△); [IB]₀ = 0.373 M, [TiCl₄]₀ = 0.104 M, [TMPCl]₀ = 0.010 M, [pyridine]₀ = 0.104 M, CH₂Cl/*n*-C₆H₁₄ = 70/30 v/v, total volume = 32 mL, 30 min. Chemicals introduction sequence: ① ED ② solvent ③ TiCl₄ ④ TMPCl ⑤ IB. $I_{\text{eff}} \approx 93\text{--}97\%$.

Subsequently, the living nature of the TMPCl/TiCl₄/pyridine/IB/CH₂Cl-*n*-C₆H₁₄ polymerization system was examined. Figure 2 shows the results of experiments carried out by the incremental monomer addition (IMA) technique at −80 and −40°C, and by the conventional all monomer in (AMI) technique at −40°C. Details of these techniques have been described [5]. The linear \bar{M}_n versus W_{PIB} (g of PIB formed) plot passing through the origin and the associated horizontal n (moles of PIB formed) versus W_{PIB} plot at the height of I_0 (number of moles of TMPCl used) indicate living polymerization. A more thorough examination of the data obtained by the diagnostic IMA technique at −40°C hints that very slow chain transfer may operate (note the deviation of the last data from the theoretical line in this series) at this temperature.

CONCLUSIONS

A series of significant observations has been made in the course of these studies: We find that the effects of the proton trap *DtBP* and the EDs are similar and both may be used to obtain LC^+Pzn (data in Tables 1-4). In view of the presence of the unshared electron pair in *DtBP*, this conclusion is not surprising. It has been proposed that MWD narrowing is due to proton trapping by *DtBP* or by Friedel-Crafts acid-ED complexes. By the simultaneous presence of the *DtBP* and $TiCl_4 \cdot ED$ complexes, improved product characteristics in terms of conversion, I_{eff} , and MWD can be obtained. The cause(s) of this apparent synergism is unknown.

Free EDs inhibit the polymerization of IB, however, $TiCl_4 \cdot ED$ complexes are beneficial and mediate the LC^+Pzn of this monomer (data in Tables 1-4). Under certain conditions several $TiCl_4 \cdot ED$ complexes precipitate from the charge before polymerization (data in Tables 1-5). However, a relationship between the presence-or-absence of precipitate and living polymerization could not be discerned; the influence of $TiCl_4 \cdot ED$ solubility on the living polymerization is totally obscure at the present. The $TMPCl/TiCl_4/pyridine/IB/CH_3Cl-n-C_6H_{14}/-40$ to $-80^\circ C$ system was selected for a detailed series of experiments, and according to the diagnostic IMA technique, this polymerization is living.

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