

Electron pair donors in carbocationic polymerization

I. Introduction into the synthesis of narrow molecular weight distribution polyisobutylenes*

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ABSTRACT

Preparatory to a detailed presentation of a large body of accumulated information, representative data have been selected to demonstrate that well-defined narrow molecular weight distribution (MWD) ($M_w/M_n \approx 1.1$) polyisobutylene (PIB) can be readily prepared in the $M_n = 1000 - 100,000$ range in the presence of certain types of electron pair donors (EDs) under a great variety of conditions. Specifically, many initiating systems, such as dicumyl chloride/ BCl_3 , dicumyl alcohol/ BCl_3 , 2-chloro-2,4,4-trimethylpentane/ $TiCl_4$, that induce nonliving polymerizations and/or give relatively broad MWD PIBs, in the presence of suitable EDs, e.g., dimethyl sulfoxide (DMSO), dimethyl acetamide (DMA), give rise to living polymerizations and yield narrow MWD products. Evidently, by the use of select EDs various undesirable side reactions, i.e., uncontrolled initiation, chain transfer, irreversible termination, indanyl end-group formation, etc., that plague carbocationic polymerizations and which therefore yield ill-defined relatively broad MWD products, can be eliminated and well-defined narrow MWD products can be obtained. The addition of EDs to otherwise extremely rapid carbocationic polymerizations results in lower controlled rates. All these observations and beneficial effects can be explained by controlled carbocation stabilization by EDs, a subject that will be explored and discussed in detail in this series of publications.

A. INTRODUCTION

The purpose of this brief communication is to announce and briefly outline a series of significant observations whose more detailed description and discussion will be the subject of forthcoming publications. In brief, we have discovered (1) that carbocationic initiating systems that do not give rise to living polymerizations will do so in the presence of certain select EDs and will yield well-defined products of narrow MWD. Further, we have reexamined and modified propositions made earlier in regard to the mechanism of living carbocationic polymerizations(2,3). Specifically, we have concluded that the typical tert.-ester or tert.-ether/ $TiCl_4$ or BCl_3 living initiating systems most likely produce EDs during the initial stages of polymerization, ("in situ" EDs) which are the true mediators of the living mechanisms. Living carbocationic polymerizations and narrow MWD products can also be

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achieved by the addition of certain types of EDs to "conventional" or inifer systems (4,5). In conventional systems high rates and a variety of side reactions due to the very high intrinsic reactivity of the polymerization-active carbocations render difficult the synthesis of well-defined narrow MWD products (6). By the judicious addition of select EDs the high reactivity of growing cations can be reduced and side reactions such as uncontrolled initiation by protic impurities, chain transfer, intramolecular alkylation by the growing cation, irreversible chain termination, etc., can be depressed or totally eliminated. Thus under select conditions conventional nonliving isobutylene polymerizations can be rendered living, i.e., transferless and free of irreversible termination, and PIBs with very narrow MWD can be obtained. A similar approach, i.e., the stabilization of carbocations by externally added bases has been used by Higashimura et al. to achieve living polymerization of vinyl ethers (7).

B. EXPERIMENTAL

B.1. Materials

The syntheses of 2-methoxy-2-propyl-benzene (cumyl methyl ether, CumOMe) (3), 1,4-di(2-methoxy-2-propyl)benzene (p-dicumyl methoxy, DiCumOMe) (8), 1,3,5-tri(2-methoxy-2-propyl)benzene (tricumyl methoxy, TriCumOMe) (9), 1,4-di(2-chloro-2-propyl)benzene (p-dicumyl chloride, DiCumCl) (5), 2-chloro-2,4,4-trimethylpentane (TMPCl) (10) and 2,6-dihydroxy-2,4,4,6-tetramethylheptane (TMHDIH) (11) and the sources and purification of CH₃Cl, n-C₈H₁₈, IB, TiCl₄ and BCl₃ have been described (2,12). 1,4-di(2-hydroxyl-2-propyl)benzene (dicumyl alcohol, DiCumOH (The Goodyear Tire and Rubber Co.) was stirred with carbon black in methanol. Anhydrous dimethyl sulfoxide (DMSO) and dimethyl formamide (DMA) (Aldrich) were used as received.

B.2. Procedures

Polymerizations were carried out in a dry box under nitrogen in large (75 mL) test tubes or round bottom flasks, as described (2,12). Detailed concentration etc. data will be given in the text and table and figure captions. PIB molecular weight determination by GPC has been described (12). End-functionality of chlorine telechelic Cl-PIB-Cl was determined by the well established dehydrochlorination method (13). ¹H NMR spectra were taken by a Varian T-60 Spectrometer using CCl₄ solutions and TMS standards.

C. RESULTS AND DISCUSSION

Table I illustrates by a few representative results the synthesis of narrow MWD PIBs under a variety of conditions in the presence of EDs.

All the initiator systems examined in the presence of EDs yielded narrow MWD PIBs with well-defined structures whereas in the absence of EDs evidence for various side reactions were found. For instance, the polymerization of IB by the DiCumCl/BCl₃ system in neat CH₂Cl₂ at -60°C leads to 40% indanyl end groups (14), however, in the presence of DMSO this side reaction is absent and Cl-PIB-Cl with $\bar{M}_n = 2490$ and $M_w/M_n = 1.15$ is formed (see lines 1 and 2 in Table I).

TABLE I
Representative Examples Demonstrating the Effect of EDs on IB Polymerizations

Initiator	Coinitiator	IB	Temp.	Solvent	ED	Conv.	I _{eff}	M _n	M _w /M _n	Remarks		
x10 ³ mole	x10 ³ mole	mL/min	°C	CH ₂ Cl ₂ /n-C ₆ H ₁₄ , mL	x10 ³ mole	%	%					
1. DiCumCl	5.00 BCl ₃	100	15/120	-60	200/-	DMSO	10.00	~100	92	2490	1.15	Telechelic product, $\bar{P}_n=2$
2. DiCumCl	0.65 BCl ₃	3-2	0.2/NA	-60	CH ₂ Cl ₂	50 mL	none	NA	105 ^a	2200 ^a	NA	~40% side product (14)
3. DiCumOH	0.31 BCl ₃	6-6	0.5/60	-60	25/-	DMSO	0.66	~100	97	1450	1.49	Telechelic product, $\bar{P}_n=2$
4. CumOH	7.50 BCl ₃	9-0	12/30	-50	CH ₂ Cl ₂	50 mL	none	~100	26	3650	1.90	Side products (15)
5. TMPCl	0.29 BCl ₃	6.3	1.5/90	-40	25/-	DMSO	0.28	37	98	1270	1.35	-
6. TMPCl	0.29 BCl ₃	6.3	1.5/90	-40	25/-	none	0.28	Negligible amount of polymer by uncontrolled (moisture) initiation				
7. TMPCl	0.10 TiCl ₄	1.8	4x(1/30) ^b	-40	10/15	DMA	0.10	39	94	10,400	1.05	
8. TMPCl	0.10 TiCl ₄	1.8	2x(1/30) ^b	-40	10/15	DMA	none	~100	120 ^c	11,200	1.73	
9. TMPCl	2.10 TiCl ₄	16.0	4x(11/10) ^b	-80	60/90	DMA	1.03	~100	98	15,700	1.09	
10. CumOMe	19.50 TiCl ₄	41.8	3x(14/5) ^b	-80	120/180	TiCl ₄ OMe		~100	43	3840	1.12	5 min. premixing (12)
11. CumOMe	1.26 TiCl ₄	10.0	3x(14/5) ^b	-80	60/90	in situ TiCl ₄ OMe		62	76	29,500	1.15	5 min. premixing (12)
12. DiCumOMe	0.40 TiCl ₄	1.2	10x(6/15) ^b	-80	60/90	in situ TiCl ₄ OMe		92	97	100,400	1.19	Telechelic product, $\bar{P}_n=2$
13. DiCumCl	240 BCl ₃	1440	550/300	-85	3500/-	DMA	0-2	~100	~100	1870	1.21	Telechelic product, $\bar{P}_n=2$
14. TriCumOMe	163 BCl ₃	1950	570/240	-50	3500/-	DMSO	49	~100	82	3290	1.19	Triarm-star product, $\bar{P}_n=3$
15. TMHDIOH	71 BCl ₃	710	220/240	-45	1600/-	DMA	71	~100	93	2080	1.21	Telechelic product, $\bar{P}_n=2$

NA = Not available

a.) Molecular weight by ¹H NMR

b.) Number of IB additions (IMA technique)

c.) The larger than 100% value is due to uncontrolled initiation by moisture impurity

d.) Molecular weight by VPO

The CumOH/BCl₃ system initiates rapid IB polymerization but the product is contaminated by indanyl end groups and its MWD is relatively broad ($\overline{M}_w/\overline{M}_n = 1.9$) (15). In contrast, the DiCumOH/BCl₃/DMSO system gives well-defined narrow MWD product (see lines 3 and 4 in Table I). (In view of the very low $\overline{M}_n = 1050$, the $\overline{M}_w/\overline{M}_n = 1.49$ value is regarded to be very narrow MWD).

The TMPCl/BCl₃ combination does not initiate IB polymerizations (4). Surprisingly, however, this system in the presence of DMSO gives controlled initiation with 100% initiator efficiency and yields narrow MWD product (see lines 5 and 6 in Table I). Figure 1 shows the ¹H NMR spectrum obtained in this experiment. Controlled initiation by (CH₃)₃CCH₂C⁺(CH₃)₂ is indicated by the presence of the tert.-butyl head-group (CH₃-protons at 0.97 ppm). The end-group is tert.-Cl (CH₃- and -CH₂-protons at 1.65 and 1.88 ppm, see assignments in Figure 1) similarly to the examples listed here and consistently found in all BCl₃- and TiCl₄-coinitiated IB polymerizations (1-3).

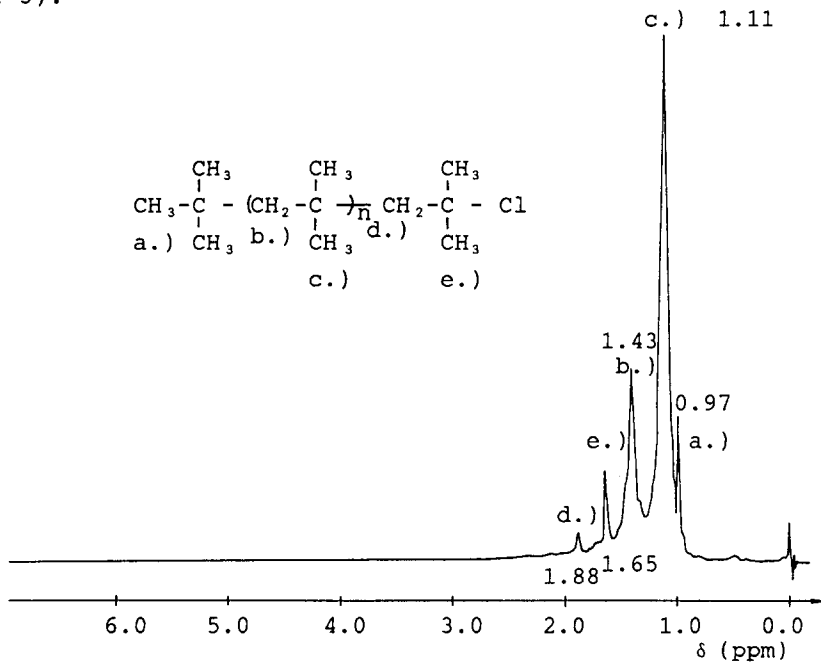
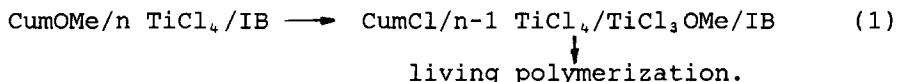


Figure 1. ¹H NMR spectrum of a PIB prepared by the TMPCl/BCl₃/DMSO/CH₃Cl system at -40°C (Table I). $\overline{M}_n = 1270$; $\overline{M}_w/\overline{M}_n = 1.35$; $I_{\text{eff}} = 98\%$

The TMPCl/TiCl₄/DMA system at -80°C and -40°C yielded PIBs with $\overline{M}_n = 15,700$ and 10,400, with $\overline{M}_w/\overline{M}_n = 1.09$ and 1.05, respectively, while in the absence of DMA this system gave relatively broad MWDs ($\overline{M}_w/\overline{M}_n = 1.73$) (see lines 7-9 in Table I).

IB polymerization initiated by CumOMe/TiCl₄ at -80°C gives rise to PIBs with narrow MWD even in the absence of

deliberately added EDs (see lines 10 and 11, Table I). We speculate that this and similar living initiating systems (e.g., cumyl acetate/TiCl₄) start the polymerization by an initial transformation to CumCl, the true initiator, plus TiCl₃OMe (or TiCl₃OAc from cumyl acetate). The latter is an "in situ" ED, i.e., an ED that arises during the initial transformation of the proinitiating CumOMe/TiCl₄ complex. The "in situ" ED changes the conventional carbocationic polymerization induced by the CumCl in conjunction with excess TiCl₄, into a living mechanism. Thus the overall reaction path conceivably proceeds by the following major steps:



These in situ released EDs, however, are less effective than properly chosen external EDs, e.g., DMSO and DMA. This proposition will be further discussed in the next publication of this series.

Low initiator efficiencies (43 and 76%, see lines 10 and 11 in Table I) are due to premixing of CumOMe and TiCl₄, because a fraction of the "aged" initiator is lost by indanyl ring formation in the first stage of the polymerization (12). In case the aim is the synthesis of a telechelic product great care should be taken to avoid this functionality-decreasing side reaction. Thus premixing was avoided and DMA was added to insure the synthesis of a high molecular weight telechelic PIB by DiCumOMe/TiCl₄ (see line 12 in Table I).

The above reactions are very slow by cationic standards (in conventional carbocationic systems polymerization is complete within seconds (6)) which indicates the presence of relatively stable active species. Undesirable temperature jumps are absent and the reaction heat is released over a controlled time period which is very beneficial in larger scale experiments. Lines 13-15 in Table I show the results of three representative preparative-scale experiments. According to these data very well defined PIB can be obtained at the liter scale.

As indicated by the above representative data and will be further demonstrated in forthcoming papers of this series, we are now able to prepare narrow MWD PIBs with practically any molecular weights in the ~500 to ~100,000 range. Figure 2 shows GPC traces of a representative set of products in the $\bar{M}_n = 1000$ to 100,000 range.

The beneficial effects outlined in this report can be explained by carbocationic stabilization by EDs. This subject will be explored in detail in further publications.

CONCLUSIONS

PIBs with narrow MWDs were synthesized in the $\bar{M}_n = 1000$ -100,000 range under a variety of conditions in the presence of EDs. The function of EDs is to stabilize reactive carbocations and thus to eliminate undesirable side reactions. The effect of EDs on the mechanism of carbocationic polymerizations and guidelines as to the selection of these compounds

to obtain controlled polymerizations and well-defined products with narrow MWDs will be discussed in further publications.

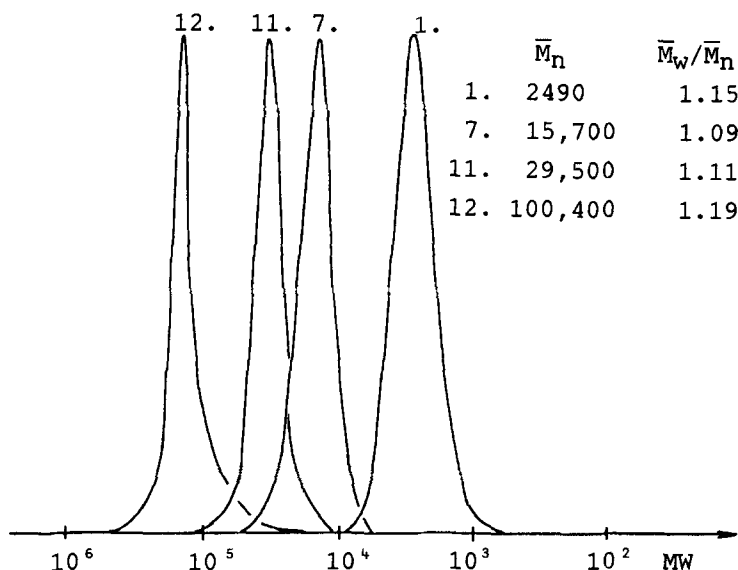


Figure 2. GPC traces of narrow MWD PIBs prepared in the presence of electron pair donors. Data in Table I

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