

Living carbocationic polymerization

LXI. Narrow molecular weight distribution polyisobutylenes prepared by esters and ketones as electron donors *

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Abstract

Electron donors (EDs) effectively mediate living carbocationic polymerizations ($LC^{\oplus}Pzn$), for example, that of isobutylene (IB). The purpose of this research was to investigate the effect of various new EDs, specifically esters and ketones on the $LC^{\oplus}Pzn$ of IB, and to determine the effect of these EDs on the molecular weight distribution, (MWD) of polyisobutylene (PIB) under various experimental conditions. Thus the $LC^{\oplus}Pzn$ of IB was effected by the dicumyl chloride (DCC)/ BCl_3 initiating system in the presence of various EDs, such as dimethyl phthalate, di-*t*-octyl phthalate, methyl benzoate, ethyl isobutyrate, dimethyl 3,3-dimethylglutarate, dimethyl terephthalate, dimethyl 5-*t*-butylisophthalate, trimethyl 1,3,5-benzenetricarboxylate; and acetophenone and benzophenone, in CH_3Cl at $-80^{\circ}C$, and the $\overline{M}_w/\overline{M}_n$ of the PIB was determined. It was found that the nature and the concentration of the ED strongly influence MWD. Under well-defined conditions in the presence of dimethyl phthalate or di-*t*-octyl phthalate, polymers with close to Poisson distribution ($\overline{M}_w/\overline{M}_n=1.03$) could be obtained.

Introduction

EDs efficiently mediate the $LC^{\oplus}Pzn$ of IB leading to narrow MWD polymer and also reduce undesired side reactions such as indane formation and initiation by protic impurities ¹. *N,N*-dimethylacetamide and dimethylsulfoxide are among familiar EDs for $LC^{\oplus}Pzn$ ¹⁻³. Recently other donors like amines and amides ⁴, such as dimethylamine, trimethylamine, dibutylamine, pyridine and its derivatives ⁵ have also been examined. Carbonyl compounds received less attention, perhaps because ethyl acetate which was the first ED examined was found to exhibit a relatively poor donor effect ⁶. In contrast to ethyl acetate, we have found many carbonyl compounds, especially some aromatic carbonyls, that are excellent EDs and produce very well-defined narrow MWD products.

The purpose of these investigations was to study the effect of various hitherto unexamined esters and ketones on the $LC^{\oplus}Pzn$ of IB, particularly on the MWD of PIBs prepared under various experimental conditions. Another objective of this work was to search for a correlation between the structure of the ED and MWD.

Experimental

Materials: Table 1 shows the chemical structures and abbreviations of the EDs used. Dimethylacetamide (DMA), methyl benzoate (MB), benzophenone (BP),

* For paper LX in this series see I. Majoros, J. P. Kennedy, et al., Polym. Bull. 31, 255 (1994)

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acetophenone (ACP), ethyl isobutyrate (EIB) were from Aldrich and were used as received. Dimethyl 5-*t*-butyl-benzene-1,3-dicarboxylate (DIPA), trimethylbenzene-1,3,5-tricarboxylate (TBT), dimethyl terephthalate (DTP), dimethyl 3,3-dimethylglutarate (DDG) were prepared by esterification from the corresponding acid in methanol using sulfuric acid as catalyst. Dimethyl phthalate (DMP) and dioctyl phthalate (DOP) were distilled under reduced pressure before experiment. The source and purification of the other chemicals used, such as IB, dicumyl chloride (DCC) initiator, BCl_3 , CH_3Cl have been described ^{7,8}.

Polymerization: A typical polymerizations experiment was carried out as follows: In a nitrogen filled stainless steel enclosure, CH_3Cl , DCC initiator, ED, and BCl_3 all in CH_3Cl solution and in this order, were premixed in a large (~70 mL) test tube and cooled to -80°C . (Final solution concentrations are given in table and figure legends). The solution turned orange-red upon the introduction of BCl_3 . After 10 minutes of aging at this temperature the polymerization was started by the introduction of neat precooled (to -80°C) IB while the reactor was vigorously agitated by a Vortex stirrer. After a minute of stirring the test tube was replaced in the -80°C bath where it was kept for about 3 hours with occasional Vortex stirrings. Since the molecular weights were kept below ~4000 g/mole, all the products were soluble in CH_3Cl and the charges were homogeneous. Polymerizations were quenched by the addition of ~2 mL prechilled methanol which immediately discharged the color. The colorless solutions were poured into 100 mL beakers and ~10 mL more methanol were added. The volatiles (CH_3Cl , unreacted monomer) were evaporated in a hood over night and the liquid polymer was washed by repeated decantation with methanol. The volatiles were evaporated in the hood over night and ~20 mL hexanes were added to dissolve the products. The hexanes solutions were filtered to remove the white boron - containing residues, the volatiles were evaporated in a hood, and the polymer was recovered. The products were washed with methanol, dried in a vacuum oven at 60°C for two days, and their weight was recorded. The colorless clear liquid products were characterized as to \bar{M}_n and \bar{M}_w/\bar{M}_n by GPC. Instruments and analytical techniques have been described in detail ⁷.

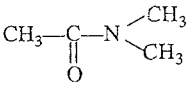
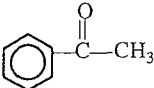
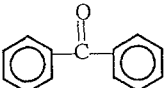
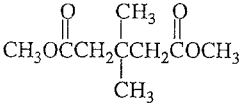
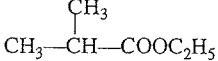
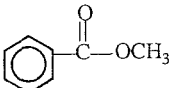
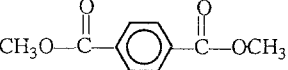
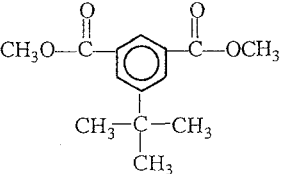
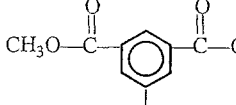
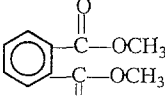
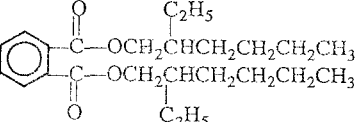
Results and Discussion

The effect of EDs on the cationic polymerization of olefins has been discussed in depth ¹. Specifically, it has been found that the polymerization of IB carried out in the presence of a variety of EDs is rendered living and that the MWD of PIBs obtained, for example, with DMSO and 2,4-pentanedione, are rather narrow, $\bar{M}_w/\bar{M}_n \sim 1.1$ ¹. We became interested in further exploring the possibility of preparing very narrow MWD PIB by the use of carbonyl-containing EDs, i.e., ketones and esters.

Table 1 summarizes the results of orienting experiments in which we compared the MWDs of PIBs obtained in the presence of the often-used ED DMA (first row) and a variety of aliphatic and aromatic ketones and esters under similar experimental conditions. The target molecular weights were kept relatively low so as to insure charge homogeneity (PIB is soluble up to $\bar{M}_n \sim 5000$ g/mole in the charges).

According to these results, several of the carbonyl compounds certainly matched the MWD narrowing efficiency of DMA and two of them, DMP and DOP, even surpassed it. This finding was followed up by investigating the effect

Table 1. Results of Orienting IB Polymerizations in the Presence of Various Carbonyl Compounds (Conditions: DCC=0.028M, ED=0.030M, IB=1.03M, CH₃Cl=25mL, -80°C, 3 hrs).

ED Structure	Abbreviations	BCl ₃	M _n	M _n /M _w
		M	g/mol	
	DMA	0.6	2810	1.13
	ACP	0.6	3160	1.13
	BP	0.6	2970	1.12
	DDG	0.5	2460	1.44
	EIB	0.6	3780	1.16
	MB	0.6	3220	1.12
	DTG	0.5	2930	1.26
	DIPA	0.5	3040	1.26
	TMBT	0.5	2740	1.27
	DMP	0.5	2520	1.08
	DOP	0.5	2440	1.08

of ED concentration on the MWD. Figures 1 and 2 show the results.

Figure 1. The Effect of DMA and DMP Concentration on the MWD of PIB. ([IB]=0.92 mol/L, [BCl₃]=0.63 mol/L, CH₃Cl 28mL, -80°C for 3 hrs [DCC]=0.02 mol/L for DMA and 0.017 mol/L for DMP)

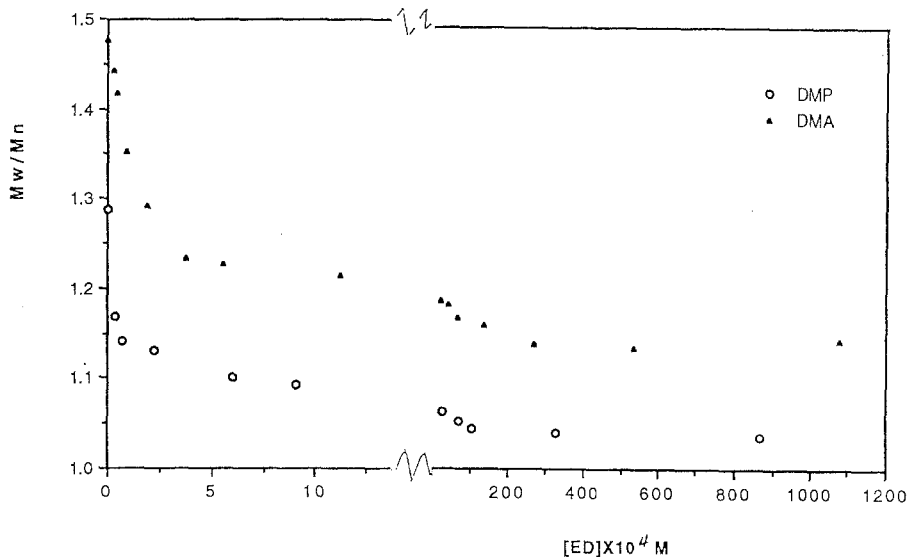
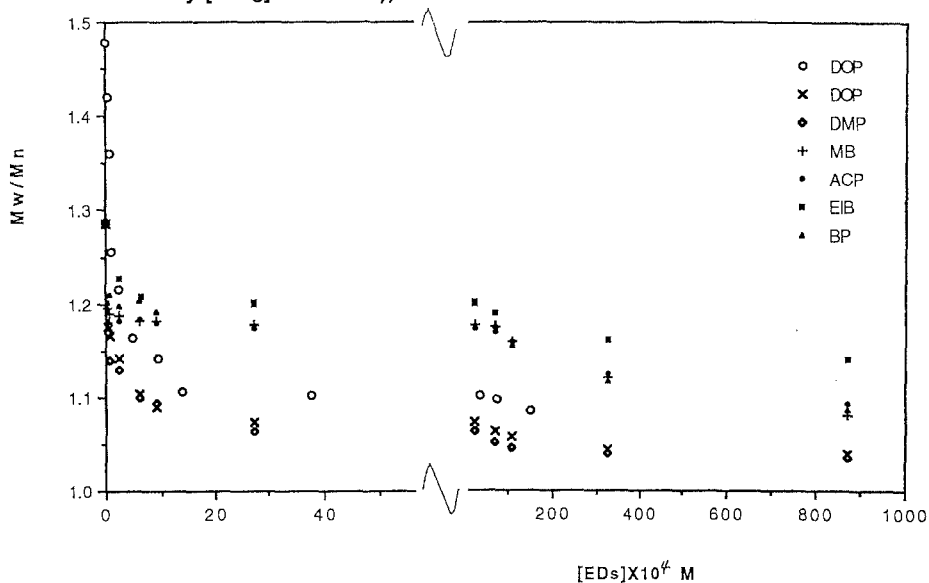


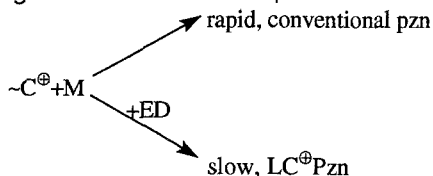
Figure 2. The donor effect of ED concentration on MWD of PIB ([DCC]=0.02 mol/L, [BCl₃]=0.63mol/L, [IB]=1.03 mol/L, CH₃Cl 25mL, -80°C, 3 hrs (in expts indicated by [BCl₃]=0.5mol/L))



In Figure 1 we contrast the MWD narrowing effect of DMA and DMP at various ED concentrations under the same polymerization conditions. Evidently, the MWDs become rapidly narrower with increasing ED concentrations until at $\sim 0.2\text{M}$ ED ($[\text{BCl}_3]/[\text{ED}]=30$) a well-defined plateau is reached. According to these data the phthalate yields a much narrower MWD product than the amide, i.e., the \bar{M}_w/\bar{M}_n obtained with the ester is 1.03-1.04 whereas that with the amide is ~ 1.14 . The M_n 's of the PIB samples obtained with the ester were uniformly somewhat higher ($\bar{M}_n=3590\pm 300$ g/mol) than those produced by the amide ($\bar{M}_n=2650\pm 200$ g/mol) because the initiator concentration used in the former experiments was somewhat lower than those in the latter (see legend to Figure 1).

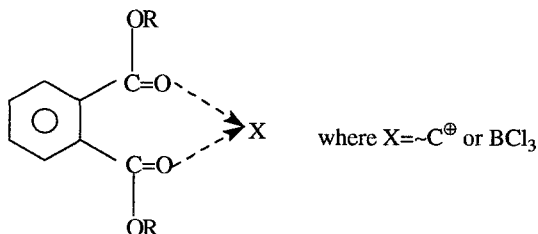
Figure 2 summarizes MWD data obtained with six carbonyl-containing EDs. Similarly to the effect seen in Figure 1, the MWDs become narrower with increasing ED concentrations. In addition, the data in this figure show noticeable differences in the MWD narrowing effect between the various EDs examined: the two phthalates, DMP and DOP, exhibit the largest effect whereas EIB, an aliphatic monoester, the lowest; the other 3 compounds fall in between these two extremes.

The shapes of the MWD versus [ED] curves suggest a characteristic kinetic effect. As discussed in detail ^{1,3}, EDs mediate $\text{LC}^\oplus\text{Pzn}$ by complexing with the propagating carbenium ion. In simplest terms



The precipitous narrowing of the MWD seen in Figs. 1 and 2 is most likely due to a rapid reduction of the rate of propagation (R_p) relative to that of initiation (R_i). Undoubtedly R_i is also diminished in the presence of EDs but the decrease in R_p far outweighs that of R_i . The strongly nucleophilic ED will of course also react with the coinitiator, $\text{BCl}_3 + \text{ED} \rightleftharpoons \text{BCl}_3 \cdot \text{ED}$, and the position of this equilibrium will affect the relative rates. For a further discussion of these matters see Ref. 1. It is of interest that Aoshima et al. have recently described a very similar kinetic phenomenon in conjunction with the $\text{LC}^\oplus\text{Pzn}$ of isobutyl vinyl ether (Figure 10 in ref. 9).

The data in Figure 2 indicate a superior MWD-narrowing effect of DMP and DOP, i.e., $\bar{M}_w/\bar{M}_n \sim 1.03$. On the other end of the scale EIB shows the smallest effect ($\bar{M}_w/\bar{M}_n \sim 1.2$) and the other four EDs fall between these two extremes. It is tempting to speculate that the strongest effect by DMP and DOP is due to relatively stable sterically and electronically favored bidentate aromatic complexes:



Less favorable complexes of monoesters (EIB, MB) and ketones (ACP, BP) give rise to relatively less stable complexes and will therefore exhibit less MWD-narrowing effect.

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