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THE ROLES OF ELECTRON DONORS IN THE CATIONIC POLYMERIZATION *

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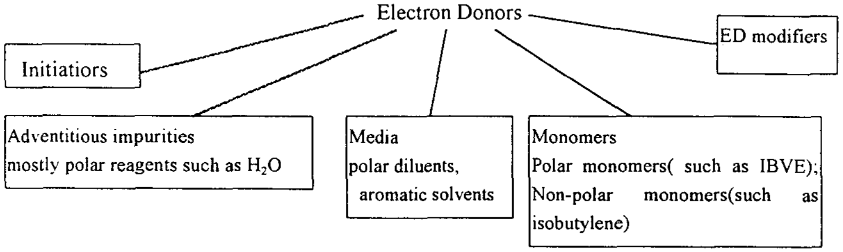
ABSTRACT

Electron donors (EDs) according to their different functions in cationic polymerization systems can be divided and summarized as follows: Initiators, adventitious impurities, aromatic solvents or polar diluents, monomers electron donor (ED) modifiers. Their behaviors and roles in the course of polymerization can be well explained in terms of complexation competition and equilibrium. In the present paper only initiators and ED modifiers are primarily investigated and discussed.

INTRODUCTION

In a broad sense, almost all polar and aromatic reagents in the cationic polymerization systems can complex with Lewis acids (coinitiators). Consequently, they all can be regarded as electron donors. (EDs).



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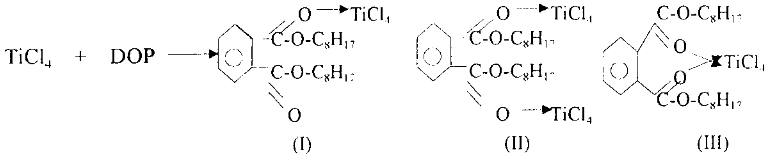
These EDs competitively complex with Lewis acids, and these reactions result in the apparent polymerization mechanism, kinetics and final polymer properties.

RESULTS AND DISCUSSIONS

- **Initiators as Electron Donors**

1. The mechanism of initiation (complexation of Lewis acids with initiators)

The initiators can play the part of initiation only after they have complexed with Lewis acids which virtually act as activators. The complexation of TiCl4 with diisoctyl phthalate (DOP) was taken for example:



The IR spectra before and after complexation are shown in Fig.1 , Fig.2 and Table 1.

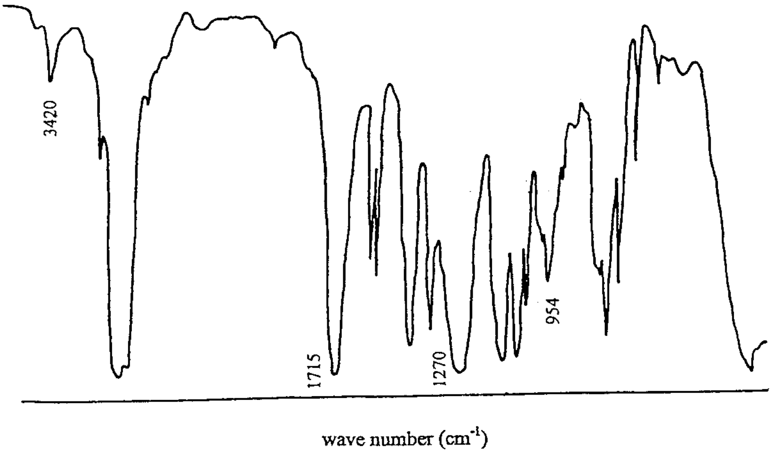


Fig. 1 IR spectrum of diisooctyl phthalate (DOP)

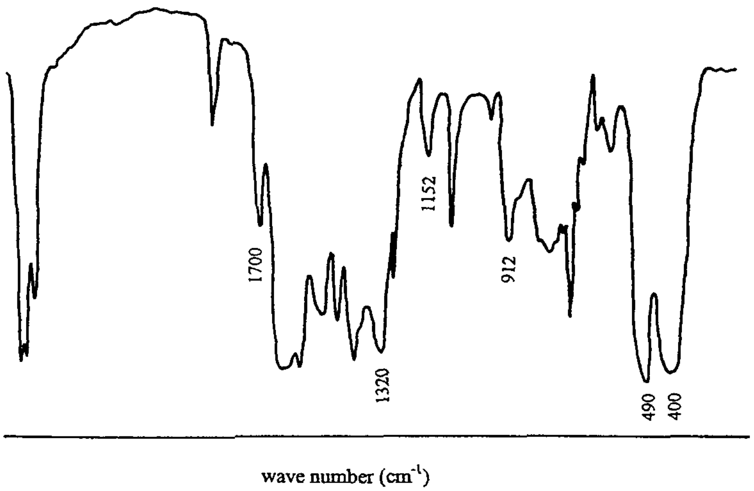


Fig. 2 IR spectrum of the complex of $TiCl_4$ with DOP

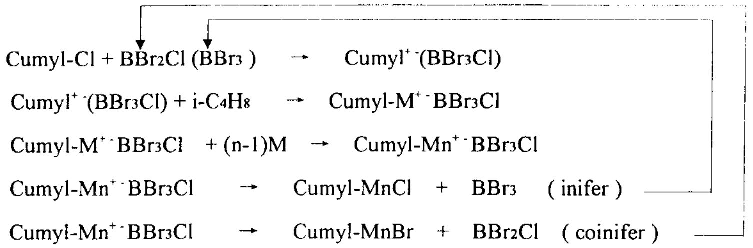
Table 1 The characteristic bands of original reagents and of their complex

sorts of different bonds	characteristic bands for $TiCl_4$ and DOP respectively (cm^{-1})	characteristic bands for their complex (cm^{-1})
ν (Ti-Cl)	498	400
ν (Ti-Cl)	/	490
ν (C=O)	1715	1700
ν (C-O-C)	1270	1320
	1120	1152

For $TiCl_4$, original band ν (Ti-Cl) is at 489cm^{-1}, and after complexation with DOP, it shifts to 400cm^{-1}.

For DOP, the original bands of ν (C=O) and ν (C-O-C) are at 1715cm^{-1} and 1270 cm^{-1} respectively, but after complexation, they shift to 1700cm^{-1} and 1320 cm^{-1}. These changes indicate that cationic moiety (ester group) can be excited to initiate the polymerization. However, Ti-Cl bonds in $TiCl_4$ after complexation become labile, and Cl^- is easy to loosen off and transfer from Ti atom to the growing polymer chain ends. Consequently, it can explain that even initiators containing no Cl (such as esters, ethers, alkanols) are used as initiators , still the Cl-terminated polymers are predominated.

A very interesting experiment is designed as follows: BBr_3 and cumyl chloride are selected as coinitiator and initiator. The following scheme are proposed(2).



$$\text{Cumyl-Cl} + BBr_2Cl\ (BBr_3) \rightarrow \text{Cumyl}^{+}\,{}^{-}(BBr_3Cl)$$

$$\text{Cumyl}^{+}\,{}^{-}(BBr_3Cl) + i\text{-}C_4H_8 \rightarrow \text{Cumyl-M}^{+}\,{}^{-}BBr_3Cl$$

$$\text{Cumyl-M}^{+}\,{}^{-}BBr_3Cl \ + (n-1)M \rightarrow \text{Cumyl-Mn}^{+}\,{}^{-}BBr_3Cl$$

$$\text{Cumyl-Mn}^{+}\,{}^{-}BBr_3Cl \rightarrow \text{Cumyl-MnCl} + BBr_3 \quad (\text{inifer})$$

$$\text{Cumyl-Mn}^{+}\,{}^{-}BBr_3Cl \rightarrow \text{Cumyl-MnBr} + BBr_2Cl \quad (\text{coinifer})$$

(Here M represents isobutylene)

The polymers so obtained are then characterized for halogen content by electron trapper detector attached to the chromatography. The data are listed in Table 2 .

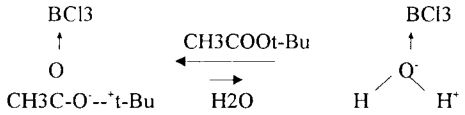
Table 2 The Molecular Weight (MW) and halogen content of PIB obtained.

No.	MN	Cl % (by wt.)	Br % (by wt.)
1	3676	0.29	1.90
2	4843	0.18	1.35

The polymers with far more Br-terminated than Cl-terminated products are obtained. The Cl / Br terminal ratio is about 1:3 . It indicates that major part of the terminals is coming from coinitiator (BBr_3) than from initiator (cumyl chloride). Although B-Br bond is somewhat more labile than B-Cl bond, this difference will not affect the comprehensive results. Thus, the "inifer" mechanism should be extended to include "coinifer".

2. Complexation Competition among the Initiating Systems

Basically, all EDs can form complexes with Lewis acids, but the roles of the complexes are different. On this account , two kinds of complexes can be divided. One kind is initiators which after complexation can give rise to active H^+ , carbenium ion to initiate the cationic polymerization and the other is inert in this respect. In this section, only the intiators as EDs are investigated. It was reported that in the CH3COOt-Bu / BCl3 / IB / CH2Cl2 system[1] , adventitious H_2O could take part in the following complexation competition.



$$\begin{array}{ccc} BCl3 & & BCl3 \\ \uparrow & CH3COOt\text{-}Bu & \uparrow \\ O & \overset{\longleftarrow}{\longrightarrow} & O^{-} \\ CH3C\text{-}O^{-}\text{--}{}^{+}t\text{-}Bu & H2O & H \quad H^{+} \end{array}$$

The both complexes are initiating systems. They compete with each other as illustrated by the above scheme and demonstrated by GPC traces, UV and IR spectra. The GPC traces changed from unimodal through bimodal and then to another unimodal feature. The growth and decline of the relative height and positions of the peaks revealed the existence of and competition between these two initiating systems. At first, only the undesired $BCl_3 \cdot H_2O$ initiating system existed i.e., in the absence of CH_3COOt-Bu. Then the two initiating systems $BCl_3 \cdot H_2O$ and $BCl_3 \cdot CH_3COOt\text{-}Bu$ coexisted corresponding to bimodal GPC traces in a certain range of $CH_3COOt\text{-}Bu$. concentration. Finally, as the concentration of $CH_3COOt\text{-}Bu$ increased beyond $BCl_3 / CH_3COOt\text{-}Bu \leqslant 2.2$(mole ratio), only $BCl_3 \cdot CH_3COOt\text{-}Bu$ system corresponding to another unimodal predominated, i.e. $BCl_3 \cdot H_2O$ system was finally displaced completely by the $BCl_3 \cdot CH_3COOt\text{-}Bu$ system. The living polymerization nature was demonstrated by direct proportion between conversion and Mn at $BCl_3 / CH_3COOt\text{-}Bu \leqslant 2.2$(mole ratio).

The above results were also followed and confirmed by UV and IR spectra investigation. The band ν (C=O) shift at 1730cm^{-1} in IR spectra indicated the complexation occurred at carbonyl oxygen of the ester. The intensity of band at 645cm^{-1} which was assigned to $BCl_3 \cdot H_2O$ gradually diminished as $CH_3COOt\text{-}Bu$ increased and vanished finally at the $BCl_3 / CH_3COOt\text{-}Bu$ ratio equaled to around 1.0. In UV spectra, the band at 319.8nm was assigned to $BCl_3 \cdot H_2O$ complex, while the band at 232.4 nm was assigned to $BCl_3 \cdot CH_3COOt\text{-}Bu$ complex and corresponding changes were also observed as those changes in IR spectra.

Very similar feature was observed in another experiment by employing Cl_2 / $TiCl_4$ /IBVE / $C_6H_5CH_3$ system. Fig.3 showed the competition between $TiCl_4 \cdot Cl_2$ and $TiCl_4 \cdot H_2O$ complexes in UV spectra. Band at 270.6 nm was obviously related to $TiCl_4 \cdot H_2O$ complex because this peak increases drastically while 20 ppm of H_2O was added and it almost vanished completely by introducing a proper amount of Cl_2 (~ 10^{-4}M).

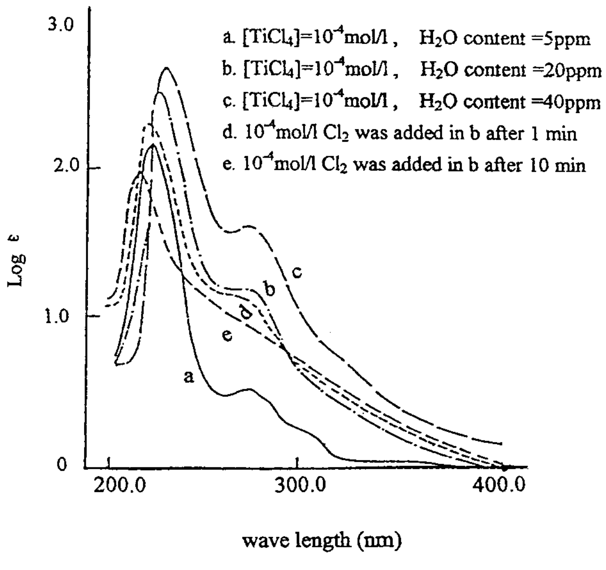
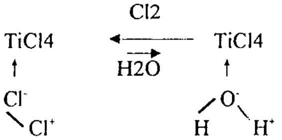


Fig. 3. UV Spectra of the complexation competition between $TiCl_4 \cdot Cl_2$ and $TiCl_4 \cdot H_2O$. Solvent: Hexane. Room temperature

This competition can be expressed by the following scheme:



From above mentioned two examples, it is clear that initiators at first must play the role of conquering or eliminating the effect of undesired initiating complex, by competitive complexation, they played the part of impurities scavenger in addition to initiation. They also possess certain role of ED modifiers, e.g., the MWD becomes more narrow and Mn was direct proportional to conversion as initiators increase.

- **ED modifiers**

ED modifiers here are specially defined as those electron donors that in the course of cationic polymerization play the role of prolonging the life and improving the selectivity of polymer growing chain (living chain) . Cl_2 / $TiCl_4$ / IBVE / n-hexane system is selected and dioxane (DOX) is used as ED modifier. Its effects can be seen in the Table 3.

The general trend is that as DOX increases, the conversion slows down, the Mn gets lower and MWD turns out to be more narrow. It is seen in the I zone, the three parameters (conversion, Mn , MWD) change noticeably with DOX concentration, and this feature very probably is due to the reaction between DOX and the initiating system $Cl_2 \cdot TiCl_4$, and in the II zone the change of the three parameters with increase of DOX concentration is insignificant and this situation is probably resulting from the strong solvation of DOX surrounding the PIBVE growing chains.

Table 3 The effect of DOX on the cationic polymerization of IBVE in CH2Cl2

No.	Zone	[DOX] / [Cl2]	tp (hr.)	Conv.(%)	MN	MWD
1	I	0	2	98.12	22000	1.78
2		1.0	2	96.87	18200	1.64
3		1.3	2	92.32	17100	1.49
4		1.6	2	91.37	16800	1.44
5		1.9	2	91.25	18500	1.38
6		2.2	2	90.89	16000	1.34
7	II	122	6	90.23	14600	1.05
8		244	6	83.52	12800	1.03
9		488	6	70.75	10100	1.02
10	III	1500	96	/	/	/

Conditions: V_{IBVE} =2ml, $[Cl_2]=4.8\times10^{-3}M$,$[TiCl_4]=9.6\times10^{-2}M$, V_{total} =32ml,Tp =-50°C
solvent: CH_2Cl_2

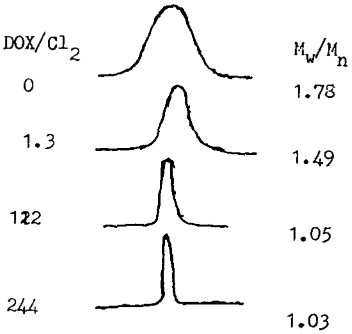


Fig .4

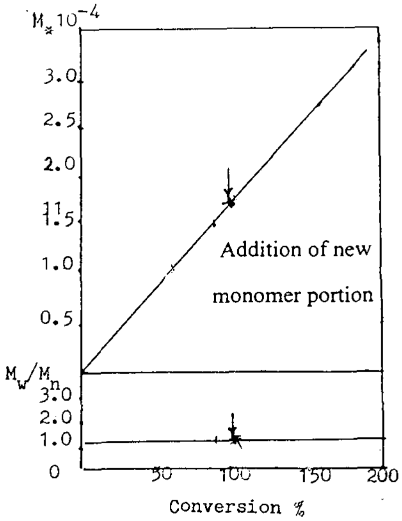


Fig. 5

Figure 4. The change of MWD with increase of DOX/Cl_2 mol ratio.

Figure 5. The change of Mn and MWD with conversion

Conditions Cl_2 / $TiCl_4$ / IBVE / -50℃ / DOX / CH_2Cl_2 system,$[DOX]/[Cl_2] \leqslant 122$

In order to get more insight into the role of DOX, two groups of experiment were carried out. One group was for the reaction of DOX with initiation system i.e. in the inititation step and another group was for the reaction of DOX with PIBVE growing chain i.e. in the propagation step.

In the zone II, the polymerization is living in nature. This can be demonstrated by that new monomer portion addition can resume the polymerization and, in addition, the color of the reaction system remains unchanged(4).

1. Reaction between DOX and initiating system

Table 4 UV spectra for $TiCl_4$, Cl_2, DOX and their reaction products

Reagents	λ max (nm) [log ε]		variation of λ max at 267nm
$TiCl_4$ in n-hexane	220.8	[3.152]	band at 267nm coexists
$TiCl_4 + H_2O$	267.0	[2.214]	band at 267nm alone exists
$TiCl_4 + Cl_2$	215.6	[2.050]	band at 267nm diminishes
$TiCl_4$ + DOX	217.4	[2.718]	band at 267nm.diminishes
$TiCl_4 + Cl_2$ + DOX	214.8	[1.977]	band at 267nm almost vanishes
Cl_2 + DOX	218.0		no reactions occur

From this Table, and Figure 6 it can be seen:

1. All Cl_2, DOX, H_2O can complex with $TiCl_4$ and band at 215.6nm, 217.4nm and 267.0nm are assigned to these complexes respectively.
2. Both Cl_2 and DOX can play the role to suppress or eliminate the formation of the complex $TiCl_4 \cdot nH_2O$.
3. The order of stability of these complexes is $TiCl_4 \cdot Cl_2 > TiCl_4 \cdot DOX > TiCl_4 \cdot nH_2O$.
4. DOX plays the role of modifying the initiating system by stabilizing it and further suppressing the formation of $TiCl_4 \cdot nH_2O$ complex.

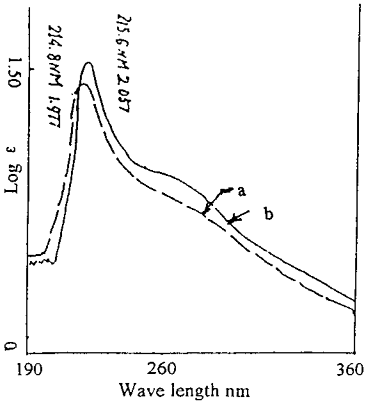


Fig 6 The effect of DOX on Cl_2, $\cdot TiCl_4$ initiation system in n-hexane solution.(0℃).

Solid line: initiation system. Cl_2, $TiCl_4$

Dotted line: initiation system + DOX

2. Reaction of DOX with PIBVE growing chain ends

Table 5 UV spectra of DOX , PIBVE and their reaction product

Item / Solvents	PIBVE growing chain		PIBVE growing chain end + DOX	
	λ max (nm)	log ε	λ max (nm)	log ε
n-hexane	214.8	2.799	217.0	3.328
n-hexane + toluene	219.4	2.543	222.4	2.736

From Table 5 and Fig.4, it can be concluded that DOX in the propagation step plays the part of solvation and simultaneously suppresses the role of H_2O which appears as $TiCl_4$ complex at 267.0nm, probably due to the shift of equilibrium to the side of $TiCl_4$ DOX and also suppress chain transfer reaction, eliminate the conjugated double bonds of the polymer end obtained as it was reported previously by us$^{(4)}$.

This feature indicates that the role of DOX in initiation step is competiting with side reactions (including complexation with undesired impurities), overcomes them and leaves only single sort of initiating system. In the meantime, DOX also stabilizes the carbocation by

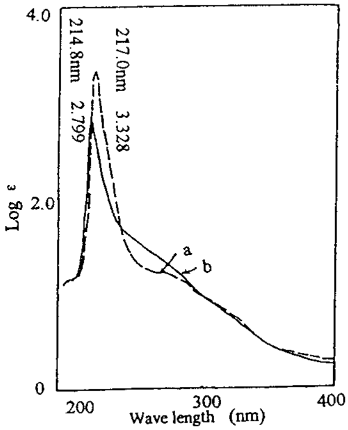


Fig.7 The effect of DOX on PIBVE growing chain end in n-hexane solution.(0℃).

Solid line: PIBVE growing chain ends (b)

Dotted line: PIBVE growing chain + DOX (a) solvation and thus slows down the polymerization rate and leads to more narrow MWD as well as lower MW, i.e. to modify the growing chain leading it less active, more selective or more living in nature.

Conclusions

1. Cationic polymerization systems are full of complexation competition and equilibrium.
2. Initiators are special kinds of electron donors. They can complex with Lewis acid , activated by them and give rise to H^+, C^+ etc., to initiate cationic polymerization, but if living cationic polymerization is expected, they must first of all compete with other active impurities (e.g. polar impurities that can give undesired initiating species) to overcome their effects in order to leave only desired single initiating system. i.e. single kind of active site.
3. ED modifiers are powerful agents to achieve living cationic polymerization. They take part in suppressing the undesired effects of certain polar impurities through complexation competition and stabilizing the growing chain ends by solvating.

References

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