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The role of complexation in living cationic polymerization with Lewis acid/ester systems

I. Living cationic polymerization of isobutyl vinyl ether (IBVE)

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Abstract

Higashimura reported living cationic polymerization by the CH3COOEt/AlEtCl2/C6H5CH3 /IBVE system, however, the mechanism was obscure and the high mole ratio of CH3COOEt/ AlEtCl2 (50/1) was unusual. To elucidate these facts the AlEtCl2·CH3COOEt complex was investigated in detail by ^{1}H-NMR, IR and UV spectroscopies. It was found that CH3COOEt was the true initiator, AlEtCl2 the coinitiator, and the ester bond the active bond. UV spectra show complexation competitions of AlEtCl2 with C6H5CH3, CH3COOEt and H2O. Living polymerizations occur only when the CH3COOEt/AlEtCl2 ratio is sufficiently high. The growing bands from 324 to 327nm correspond to living complexes and indicate constant monomer insertion and complex formation during propagation.

Introduction

Living polymerization is a convenient way to achieve polymer design. Some 30 years ago Szwarc first published the living anionic polymerization of styrene.(2,3) Since then numerous papers have been published in this field and it turned out to be also of great commercial interest. Living cationic polymerization succeeded only very recently. T.Higashimura et al.(4) in 1984 developed living polymerization of IBVE with the HI/I2 system and two years later he also successfully employed the CH3COOEt/ALEtCl2(1) and dioxane/AlEtCl2(5) systems for the same purpose. Almost simultaneously J.P Kennedy reported on the living carbocationic polymerization of isobutylene (IB) with the similar CH3COOt-Bu/BCl3 system.(7,6) These were true breakthroughs in the field of cationic polymerization. Neverthless a direct demonstration of living mechanism was still lacking and the tremendous difference in their ester/Lewis acid ratios used also remains a puzzle. This paper concerns primarily the role of complexation, gives direct demonstration of living mechanism, and describes necessary and sufficient conditions for achieving living cationic polymerization with Lewis acid/ester system.

Experimental

A.Materials. IBVE (A.R. Swiss). It was washed with dilute NaOH and water and dried with solid KOH. Toluene (C.P.) was dried with 4A molecular sieves at least for one week. All reagents were refluxed in the presence of CaH2 and distilled before use. AlEtCl2 (Yanshan Petrochemical Co.) was used as receivd.

B.Instruments. UV spectrometer, Shimadzu UV-260(Japan). IR spectrometer, Shimadzu IR-420(Japan). ^{1}H-NMR, EM-360(Germany). GPC, Waters 150C, Columns(10^3, 10^4, 10^5,Styragel). VPO(Knauer, Germany).

C.Procedures. Polymerization was carried out under dry nitrogen in repeatly baked three-necked flasks equipped with a stirrer. The polymerization temperature was maintained by a thermostat. Reagents were added by a dry syringe by the following sequence: solvent, ester, IBVE, Lewis acid. Polymerization was terminated by methanol. The product was washed with dilute HCl and water, and finally dried under vacuum.

D.Polymer sample preparation. Polymer samples were first subjected to repeatedly dissolving, precipitating and drying under vacuum to constant weight. The sample so obtained was examined by UV spectroscopy. The absence of IBVE residues was indirectly demonstrated by the absence of toluene, the boiling point of which is 34°C higher than of IBVE, and because the amount of toluene used was 7.5 times larger than that of IBVE. (Fig.3)

Results and Discussion

1. Structure characterization of the chain terminal

Fig.1 IR spectrum of PIBVE

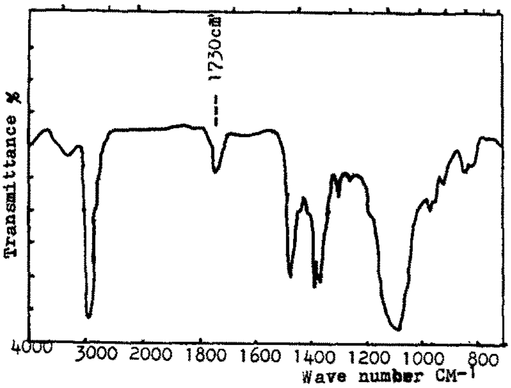


Figure 1 gives the IR spectrum of PIBVE and shows all the characteristic absorption bands of standard PIBVE, except at 1730cm^{-1} which is assigned to a carbonyl group. The polymer sample was then examined by ^{1}H-NMR (Figure 2). The spectrum shows resonauces at 1.9 ppm

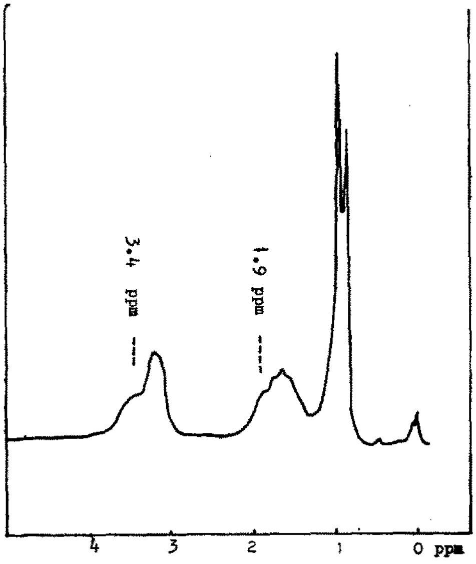


Fig.2 ^{1}H-NMR spectrum of PIBVE

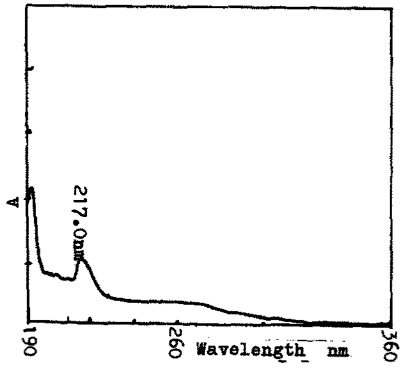
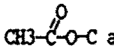
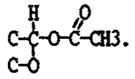


Fig.3 UV spectrum of the PIBVE

and 3.4 ppm characteristic of  $CH_3\text{-}\overset{O}{\overset{\|}{C}}\text{-}O\text{-}C$ and  $C\text{-}\underset{C\text{-}O}{\overset{H}{C}}\text{-}O\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_3$. UV spectroscopy was used to distinguish the ester from ketone (the absorption bands of carbonyl groups of ester and ketone appear at 200-220nm and 280-300nm, respectively). Figure 3 shows a band at 217nm, indicating that the carbonyl group can only be due to an ester.

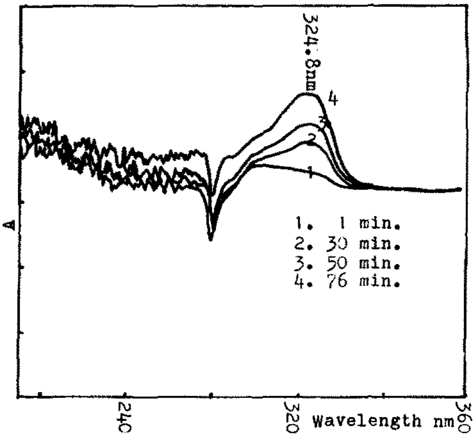
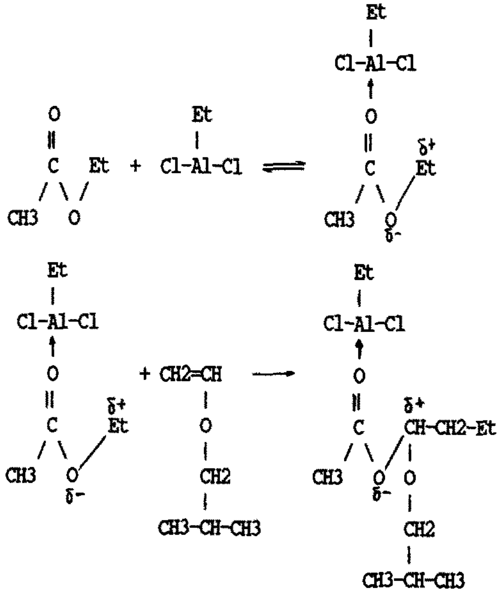


Fig.4 UV spectra of the $CH_3COOEt/AlEtCl_2/$ IBVE / toluene system at different polymerization times 1. 1 min. 2. 30 min. 3. 50 min. 4. 76 min.

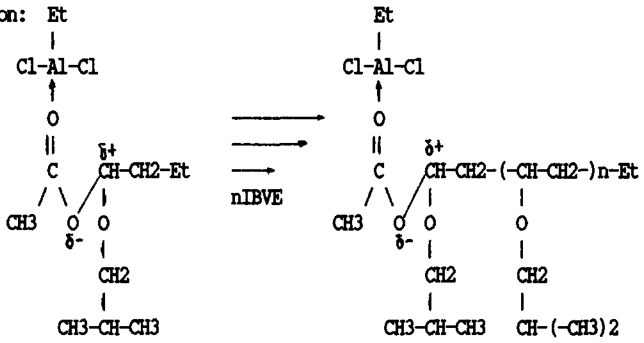
Reference: Mixture of toluene and CH_3COOEt

Figure 4 gives the UV spectra of polymers obtained at different polymerization times. The spectra show gradually growing absorptions around 324nm indicating the increasing formation of polymer ester/AlEtCl2 complexes during the polymerization. In addition, the valley around 280nm diminishes as the absorption at 324nm increases, indicating that the chain propagates at the expense of IBVE. Adopting Kennedy's mechanism (7) the living polymerization of IBVE by the CH3COOEt/AlEtCl2 system can be written as follows:

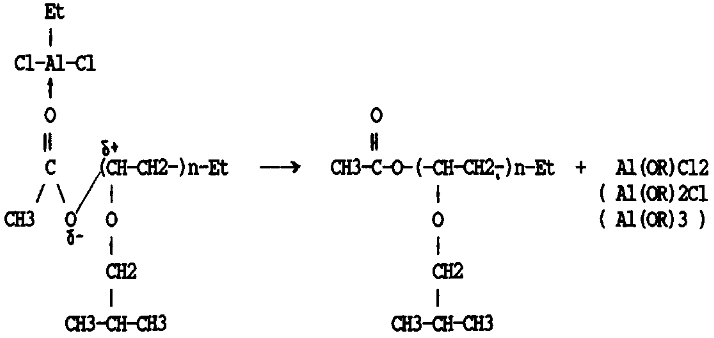
Initiation:



Chain propagation:



Chain termination (ROH as terminator):



According to Aoshima and Higashimura (9) oligomerization of IBVE gives a chain end containing a double bond arising from chain transfer. The ester group may be due to our different system, reaction conditions, and termination modes. Besides, chain transfer and chain termination should be absent in true living polymerization, so this model is not applicable to our living polymerization system.

2. Living IBVE polymerization with Lewis acid/ester systems

We have investigated IBVE polymerization by the use of various CH3COOEt/AlEtCl2 ratios. Table 1 shows the experimental conditions and observations.

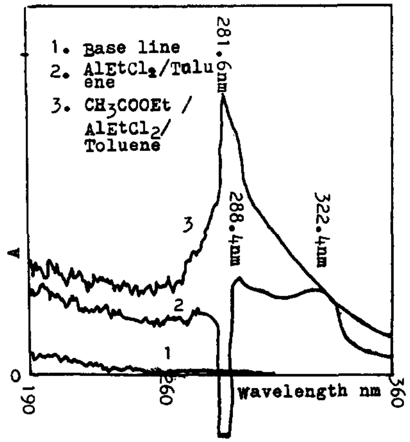


Fig. 5 UV spectra of
3. CH3COOEt/AlEtCl2/ toluene
2. AlEtCl2/toluene
1. Base line

TAB.1. Results of the Polymerization of IBVE*

CH3COOEt/AlEtCl2	0:1 control	1:1	10:1	30:1	50:1
Time required for color change	instant-aneous	0.5 min	20 min	——	——
Color of the polymn. system	brown	light yellow	light yellow	white	white
Modality	bimodal	monomodal	monomodal	monomodal	monomodal
Color of the polymer	orange	orange	orange	white	white
Mw/Mn	4-11	4-10	3-4	2-3	< 2

*Initiation system CH3COOEt/AlEtCl2, [IBVE] 10%(Vol), [AlEtCl2] 20mM, 25°C, Toluene

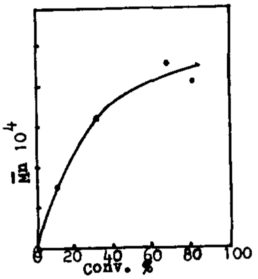


Fig.6 Mn vs. conv. of PIBVE initiated by CH3COOEt/AlEtCl2 30/1

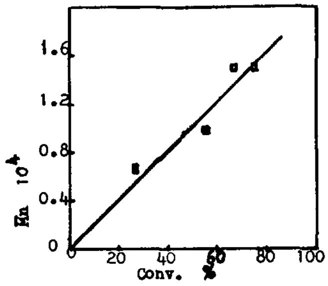


Fig.7 Mn vs. conv. of PIBVE initiated by CH3COOEt/AlEtCl2 50/1

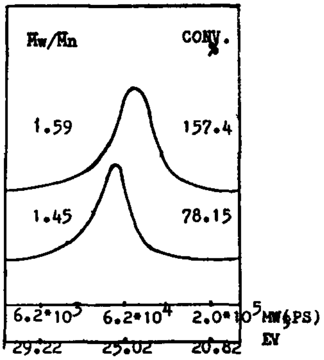


Fig.8 GPC of PIBVEs prepared by IMA technique(6)

Figure 5 shows the characteristic absorption bands of AlEtCl2•toluene and AlEtCl2•CH3COOEt complexes at 284nm and 322nm respectively. The valley observed in some of the curves is due to more transparent sample solutions than the reference solution. IBVE does not form a complex with AlEtCl2 showing absorption bands within this range. Absorbance at 309nm is assigned to the AlEtCl2•H2O complex.(8) The complex of AlEtCl2•H2O can also initiate IBVE polymerization, as seen from the control experiment in Table 1. The last traces of moisture are too difficult to remove from the system, therefore, some polymer is still obtained in the absence of ester. The ratio of CH3COOEt/AlEtCl2 affects

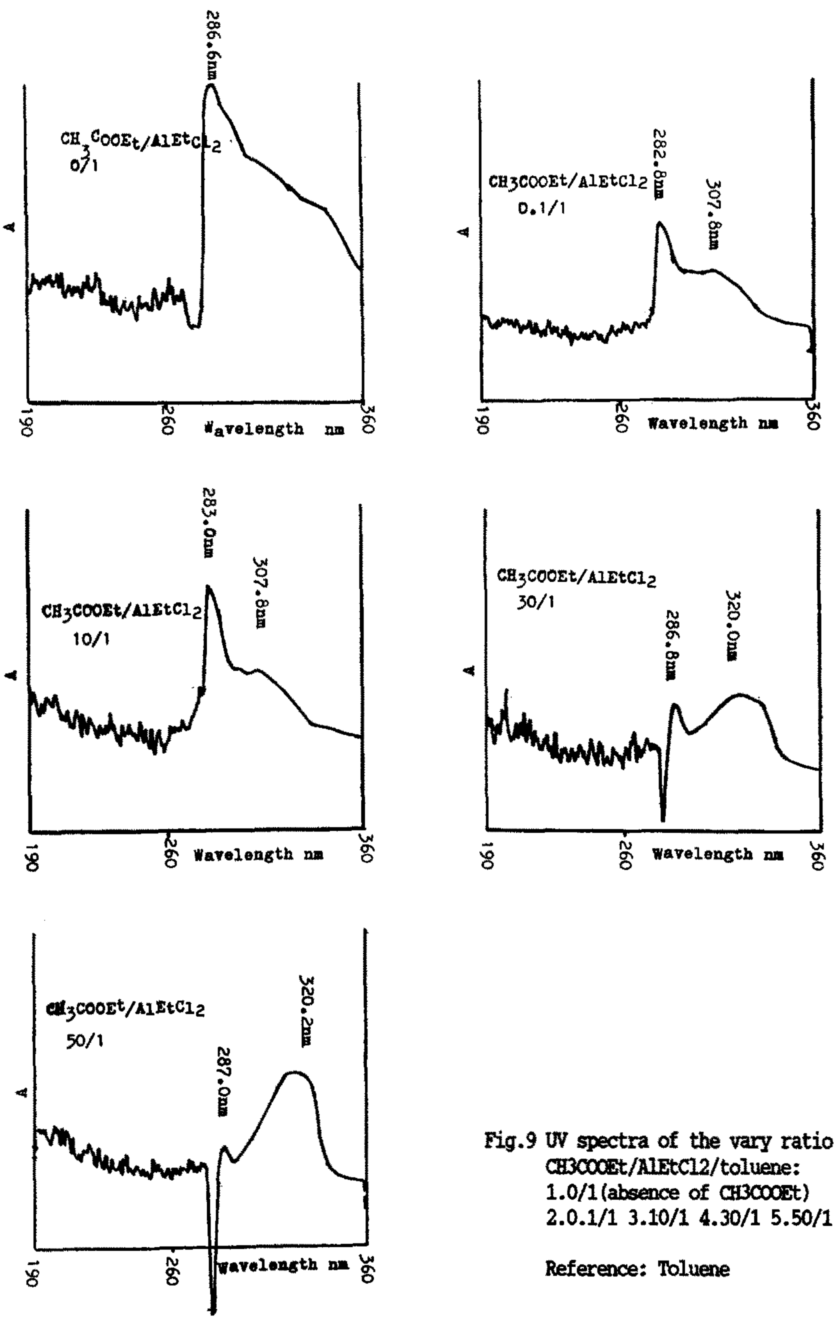


Fig.9 UV spectra of the vary ratio
CH3COOEt/AlEtCl2/toluene:
1.0/1(absence of CH3COOEt)
2.0.1/1 3.10/1 4.30/1 5.50/1

Reference: Toluene

the polymerization and is worthy of investigation in detail. As shown in Table 1 when CH3COOEt/AlEtCl2 < 50, the polymerization is nonliving. Figure 6 shows that at CH3COOEt/AlEtCl2 = 30 the Mn versus conversion plot is not linear. The MWDs are 2-3. In contrast, as indicated by the data in Figure 7, when the CH3COOEt/AlEtCl2 ratio is > 50, the system becomes living in nature and the MWDs obtained at different conversions are narrow (<2) throughout the whole polymerization process. In addition, the living nature has also been demonstrated by resuming the polymerization with fresh monomer addition, as shown in Figure 8.

In order to elucidate why such a large excess of CH3COOEt is needed, a series of UV spectra at different CH3COOEt/AlEtCl2 ratios were investigated in detail. Figure 9 shows the gist of these experiments. By increasing the ratio, the absorptions at 282nm and 197nm due to the AlEtCl2•toluene and AlEtCl2•H2O complexes either diminish or disappear completely. This clearly indicates a complexation competition. If the concentration (or ratio) of CH3COOEt (or CH3COOEt/AlEtCl2) increases beyond a certain critical value, depending on the nature of solvent or adventitious impurities in the system, then living polymerization is possible.

Conclusions

1.CH3COOEt/AlEtCl2 complex is the true living initiating species. CH3COOEt is the initiator and AlEtCl2 the coinitiator.

2.There are complexation competitions among the various complexes, such as AlEtCl2•toluene, AlEtCl2•H2O and AlEtCl2•CH3COOEt.

3.The necessary conditions for living IBVE polymerization with the CH3COOEt/AlEtCl2 system is that the Lewis acid should play two roles: 1) stabilizing the counterion by complexation, so as to prevent chain transfer and termination, and 2) activating the labile O-Et bond in the initiator.

The sufficient condition for living IBVE polymerization is that the true initiating complex shoud outcompete the other initiating complexes and this can be achieved by controlling the CH3COOEt/AlEtCl2 ratio.

Acknowlegment

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