

CATIONIC POLYMERIZATION OF 1,3—PENTADIENE INITIATED BY ORGANIC AZIDE/ Et_2AlCl

PENG Yuxing(彭宇行) DAI Hansong(戴汉松)
LIU Jialin(刘佳林) and CUN Linfeng(寸琳峰)

(Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences, Chengdu 610041)

ABSTRACT

The cationic polymerization of 1,3-pentadiene was initiated by the organic azide/ Et_2AlCl initiating system in CH_2Cl_2 and *n*-hexane. The polymerizations were also carried out in parallel with organic chloride/ Et_2AlCl and Et_2AlCl alone for comparison. The Et_2AlCl -induced polymerization gives a low yield while the polymerization initiated by organic chloride/ Et_2AlCl produces mainly insoluble product. In contrast, the polymerization with azide/ Et_2AlCl has a high conversion and the resulting polymer having a high molecular weight is totally soluble. The SEC spectra of the polymers have clearly shown the differences between these initiating systems.

INTRODUCTION

The cationic polymerization of 1,3-pentadiene (PD) has not yet been thoroughly studied in spite of its uses in the production of C_5 petroleum resin.^[1] In fact, the application for the cationic homopolymerization of PD is quite limited because of the low molecular weight of polypentadiene (PPD) and the formation of insoluble crosslinked product in many polymerization systems.

Several Lewis acid-based initiators^[2-4] have been used for the polymerization of PD. The insoluble crosslinked products are always generated and the conversions appear incomplete. Aluminum triflate, a novel salt of superacid HOTf , has also been employed for this polymerization.^[5,6] This initiator can avoid the generation of insoluble products and give a high yield. But the resulting PPD has

a relatively low molecular weight.

We have recently made an interesting observation that the organic azide/ Et_2AlCl combination is an efficient cationic initiating system. In the present communication we report briefly the results of the polymerization initiated by two azide/ Et_2AlCl systems. Bis-1, 4-(1-azido-1-methyl-ethyl)-benzene (BAMEB) was prepared according to reference [7] and trimethylsilyl azide (TMSA) was available from Aldrich. For comparison the polymerization was also carried out with Et_2AlCl alone and two organic chloride/ Et_2AlCl systems where the two chlorides are allyl chloride (AllylCl) and cumyl chloride (CumCl).

Polymerization in methylene chlorides

It is well known that Et_2AlCl itself is a weak cationic initiator (cocatalysis with residual H_2O , i. e., $\text{H}_2\text{O}/\text{Et}_2\text{AlCl}$ initiation) but the cationogen/ Et_2AlCl combination turns to an active initiating system. For example, organic chlorides were often used in complexation with Et_2AlCl in order to enhance the initiating activity. Table 1 illustrates the results of the polymerizations of PD in CH_2Cl_2 initiated by Et_2AlCl both in the absence and in the presence of two azides (BAMEB and TMSA) and two chlorides (AllylCl and CumCl):

Table 1 Polymerizations of PD in methylene chlorides^{a)}

No.	Initiating system	Reaction time	Conversion (%)			$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$
			Total	S	I		
1	" H_2O "/ Et_2AlCl	18h	22	22	0	4000	2.7
2	BAMEB/ Et_2AlCl	18h	76	76	0	6000	2.6
3	TMSA/ Et_2AlCl	18h	61	61	0	6000	2.5
4	AllylCl/ Et_2AlCl	30min*	72	22	60	3900**	2.5**
5	CumCl/ Et_2AlCl	30min*	78	14	64	3000**	2.6**

S-Soluble polymer; I-Insoluble product (crosslinked). * Polymerizations blocked by insoluble product in 30 min. ** for soluble polymer. ^{a)}[PD]: 2.3 mol/L; [Initiator]: 10^{-2} mol/L; [Et_2AlCl]: 7×10^{-2} mol/L; Reaction temperature: 20°C

As evidenced in Table 1, " H_2O "/ Et_2AlCl initiating system gives a relatively low yield (No. 1). Chlorides/ Et_2AlCl appear much more effective and give higher conversions (No. 4 and 5) but these initiating systems induce the crosslinking reaction and produce insoluble polymers. On the other hand, the polymerizations induced by BAMEB/ Et_2AlCl and TMSA/ Et_2AlCl have much higher conversions

and generate a totally soluble polypentadiene. In addition, PPD produced by these two systems has a higher molecular weight compared with PPD prepared by chlorides/ Et_2AlCl and Et_2AlCl alone. Therefore, azide/ Et_2AlCl seems to be an efficient initiating system that produces a totally soluble high molecular weight PPD with a high conversion. All these observations are among the results that has long been seeking for by the investigators in this field.

Polymerization in n-hexane

We have also carried out the polymerizations in n-hexane, a less favorable solvent than CH_2Cl_2 for the cationic polymerization of PD.^[5,6] The results are summarized in Table 2:

Table 2 Polymerizations of PD in n-hexane^{a)}

No.	Initiating system	Reaction time	Conversion(%)			$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$
			Total	S	I		
6	"H ₂ O"/ Et_2AlCl	18h	7	7	0	3000	3.1
7	BAMEB/ Et_2AlCl	18h	54	54	0	5100	2.8
8	TMSA/ Et_2AlCl	18h	8	8	0	2800	3.0
9	AllyCl/ Et_2AlCl	30min*	83	21	62	3400**	3.2**
10	CumCl/ Et_2AlCl	30min*	83	24	59	3500**	3.0**

S-Soluble polymer; I-Insoluble product (crosslinked). * Polymerizations blocked by insoluble product in 30 min. ** for soluble polymer. ^{a)}[PD]: 2.3 mol/L; [Initiator]: 10^{-2} mol/L; [Et_2AlCl]: 7×10^{-2} mol/L; Reaction temperature: 20°C

The polymerization induced by Et_2AlCl in n-hexane gives a very low yield and the presence of TMSA fails to give any improvement. However, the polymerization induced by BAMEB/ Et_2AlCl results in a high conversion. The resulting polymer has a high molecular weight and is totally soluble. In contrast, two chloride/ Et_2AlCl combinations give high conversions but are dominated by insoluble products.

As shown in Table 1 and Table 2, in CH_2Cl_2 the two azide-containing initiating systems, BAMEB/ Et_2AlCl and TMSA/ Et_2AlCl , are both efficient combinations for the cationic polymerization of PD. These systems produce soluble high polymers with a much higher conversion than "H₂O"/ Et_2AlCl initiating system. However, when n-hexane is used as solvent only BAMEB/ Et_2AlCl remains effective.

In Fig. 1, the SEC spectra of PPDs (No 6,7 and 10 in Table 2) are presented. These curves indicate that BAMEB/ Et_2AlCl -induced polymerization can shift PPD's SEC spectra to the higher molecular weight side.

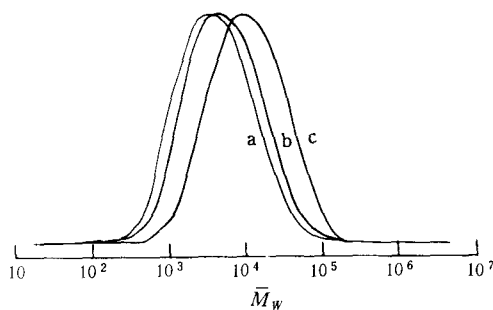


Fig. 1 SEC spectra of polypentadienes. Initiating system:

- a) " H_2O "/ Et_2AlCl (No. 6 in Table 2)
- b) $\text{CumCl}/\text{Et}_2\text{AlCl}$ (No. 10 in Table 2)
- c) BAMEB/ Et_2AlCl (No. 7 in Table 2)

Keywords:

Cationic polymerization; 1,3-Pentadiene initiator; Azide/ Et_2AlCl

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