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Effect of allylic halides on cationic polymerization of 1,3-pentadiene

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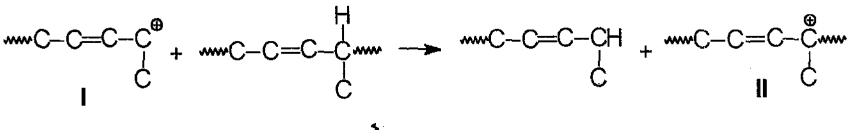
Summary

The cationic polymerization of 1,3-pentadiene (PD) initiated by $AlCl_3$ in n-hexane was carried out in the presence of allylic halides, i.e., 3-chloro-1-butene, allyl chloride, and allyl bromide. All these allylic halides strongly hindered crosslinking which is a major side reaction during PD cationic polymerization. Cyclization, another side reaction, was also reduced by the addition of the allylic halides. The influences of these halides on polymer yields and molecular weights are also discussed.

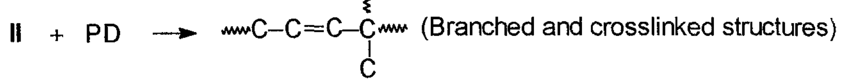
Introduction

It is well known that the cationic polymerization of conjugated dienes produces only ill-defined polymer structures that are often mixtures of linear, cyclic, branched and crosslinked structures (1), due to various secondary reactions. For example, the polymerization of 1,3-pentadiene (PD) initiated by Friedel-Crafts acids produces a partially cyclized polymer and this polymerization system is usually accompanied by the formation of insoluble crosslinked products (2-4). The protic acid-induced polymerization could avoid crosslinking but generates the polymer with a higher cyclic content (5).

In fact, crosslinking and cyclization are two characteristic side reactions which appear uncontrollable in many circumstances during the cationic polymerization of PD. Crosslinking occurs on carbocation **II** formed by the intermolecular hydride shift between the chain growing carbocation (cation **I**) and the polymer chain (6):



$$\underset{\mathbf{I}}{\sim C-C=C-\underset{C}{\overset{\oplus}{C}}} + \sim C-C=C-\underset{C}{\overset{H}{C}}\sim \longrightarrow \sim C-C=C-\underset{C}{CH} + \underset{\mathbf{II}}{\sim C-C=C-\underset{C}{\overset{\oplus}{C}}\sim} \qquad [1]$$



$$\mathbf{II} + PD \longrightarrow \sim C-C=C-\underset{C}{\overset{\wr}{C}}\sim \text{ (Branched and crosslinked structures)} \qquad [2]$$

On the other hand, cyclization takes place mainly on the pendant double bonds of 1,2-units through a cationization process (5):

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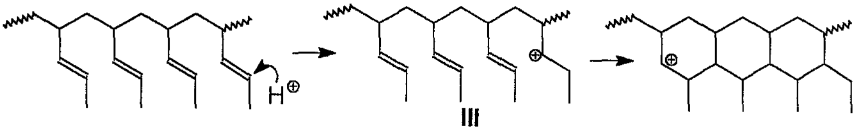
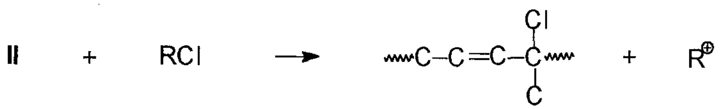


[3]

We have recently discovered that alkyl halides (RX), particularly tertiary halides, exert a strong reduction effect on the crosslinking reaction in the cationic polymerization of PD (7). We proposed that the chain transfer of carbocation **II** to the halide (equation [4]), a competitive reaction with the crosslinking reaction [2], could essentially suppress the formation of the crosslinked polymer:



$$\mathbf{II} + RCl \longrightarrow \sim C{-}C{=}C{-}\overset{Cl}{\underset{C}{C}}\sim + R^{\oplus}$$

[4]

Along with this line, we have expanded the investigation scope to other kinds of halides. The present work concerns the results of the effects of allylic halides on crosslinking and cyclization in the cationic polymerization of 1,3-pentadiene initiated by $AlCl_3$ in n-hexane.

Experimental

Materials

1,3-Pentadiene from Fluka was distilled over CaH_2. 3-Chloro-1-butene, allyl chloride, allyl bromide and n-hexane were also distilled over CaH_2. $AlCl_3$ was purified by sublimation in vacuum.

Polymerization

$AlCl_3$ was introduced in a three-necked-reactor in dry nitrogen atmosphere. The solvent and allylic halide were added and then the polymerization was achieved by introduction of PD by syringe. After a given time, the polymerization was quenched by the solvent containing a small amount of methanol. The resulting solution was filtered to remove insoluble (crosslinked) product. The filtrate was washed with water and dried by evaporation to recover the soluble polymer.

Measurements

^1H NMR spectra of the polymers were recorded by VARIAN FT-80A spectrometer. Intrinsic viscosities were determined with an Ubbelohde viscometer in toluene at 30°C.

Results and discussion

Table 1 summarizes the effects of 3-chloro-1-butene (ClBu), allyl chloride (AllyCl) and allyl bromide (AllyBr) on the polymerizations of PD at 25 °C and 0 °C, respectively. We observe that the presence of the three allylic halides substantially depressed crosslinking for PD cationic polymerization at 25°C. However, this crosslinking-depression effect becomes much weaker in the polymerization at 0°C.

As the cyclization process during PD cationic polymerization results always in the decrease of double bonds (see equation [3]), the unsaturation loss (UL), calculated from integration intensities of unsaturated and saturated protons on ^{1}H NMR spectra, has been used to describe the cyclization degree (5). Table 1 shows UL values of the polymers. We observe that the allylic halides have a reduction effect on cyclization, but this effect appears much milder than that on crosslinking. Similarly, the cyclization reduction effect of the allylic halides decreases while the temperature decreases.

Table 1. Effects of allylic halides on crosslinking and cyclization [a)]

No	Temperature (°C)	Allylic halide	Yield (%)			UL[b)] (%)
			Total	Soluble	Crosslinked	
1	25	None	85	47	38	69.5
2	25	ClBu	85	82.5	2.5	49.3
3	25	AllyCl	82	76	6	57.5
4	25	AllyBr	82	74	8	51.9
5	0	none	71	49	22	67.0
6	0	ClBu	81	68	13	60.2
7	0	AllyCl	86	67	19	63.0
8	0	AllyBr	83	60	23	62.5

a) [PD]=2mol/L, [$AlCl_3$]=5×10^{-2}mol/L, [Allylic halide]/[$AlCl_3$]=3, Reaction time: 4h, Solvent: n-hexane.
b) UL: Unsaturation loss, calculated from ^{1}H NMR spectra.

In order to further understand the effect of the allylic halide on crosslinking for the polymerization at 25 °C, we conducted a series of polymerizations at various halide concentrations. Figures 1-3 shows the results of the polymerizations in the presence of ClBu, AllyCl and AllyBr, respectively.

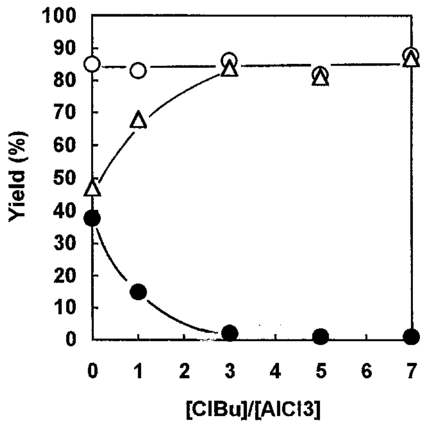


Figure 1. Effect of ClBu on crosslinking. Reaction conditions as in Table 1. ○ Total yield; △ soluble; ● crosslinked.

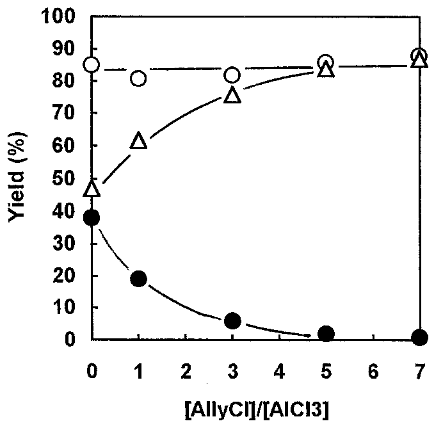
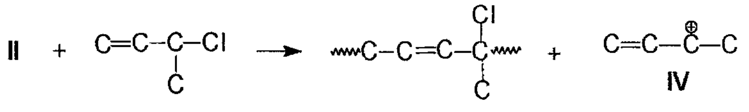


Figure 2. Effect of AllyCl on crosslinking. Reaction conditions as in Table 1. ○ Total yield; △ soluble; ● crosslinked.

We observe that all the three allylic halides can essentially reduce the crosslinking reaction and even completely eliminate the formation of crosslinked products at a high [Allylic halide]/[$AlCl_3$] ratio. The results in Figures 1-3 show also that ClBu has the strongest crosslinking-reduction effect among the three halides.

We propose a chain transfer reaction of cation **II** to the allylic halide, similar to equation [4], to explain the reduction effect of allylic halides on crosslinking. For 3-chloro-1-butene, schematically,



$$\mathbf{II} + C{=}C{-}\underset{C}{C}{-}Cl \longrightarrow \sim\!C{-}C{=}C{-}\overset{Cl}{\underset{C}{C}}\!\sim + \underset{\mathbf{IV}}{C{=}C{-}\overset{\oplus}{C}{-}C} \qquad [5]$$

The above transfer process, whose driving force is the high stability of formed carbocation **IV**, is much likely to occur (8). As this reaction is a competitive reaction to reaction [2], hence the crosslinking reaction can be reduced or even suppressed by the presence of allylic halides. Obviously, cation **IV** resulting from ClBu has the highest stability among the three cations formed from corresponding halides, ClBu gives therefore the strongest reduction effect on crosslinking. In addition, As carbocation **IV** has a structure quite similar to the chain growing cation (carbocation **I**), we suppose that newly formed cation **IV** has a similar reactivity with cation **I** and is capable to sustain chain propagation. As a result, the kinetic chain is not stopped by reaction [5] and the overall yield is not affected by allylic halides. This consideration has been fully supported by the results showed in Table 1 and Figures 1-3. The effect of allylic halides on the polymer yield appears different from that of the tertiary halides (7) which exert a strong reduction effect on polymer yields.

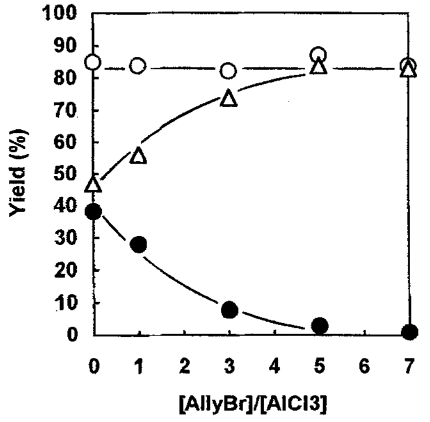


Figure 3. Effect of AllyBr on crosslinking. Reaction conditions in Table 1. ○ Total yield; △ soluble; ● crosslinked.

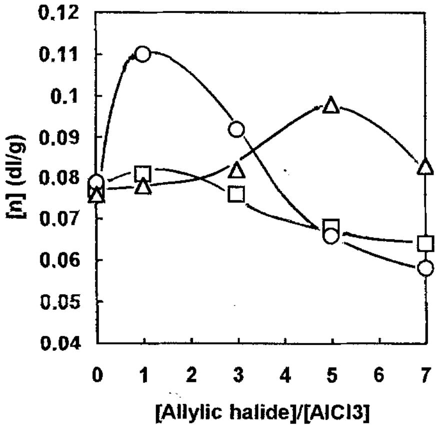
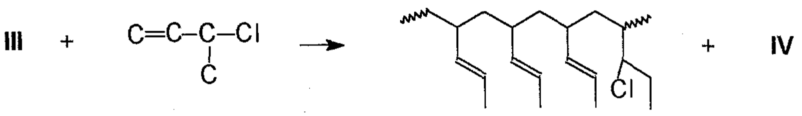


Figure 4. Effect of allylic halides on intrinsic viscosity. Reaction conditions as in Table 1. □ ClBu; ○ AllyCl; △ AllyBr.

To explain the effect of the allylic halide on cyclization, a similar transfer reaction of carbocation **III** (in equation [3]) to the allylic halide could be visualized. For example,



[6]

As we can see in Table 1, the reduction effect of the allylic halide on cyclization is much weaker than that on crosslinking. This means reaction [6] reducing cyclization might present during PD cationic polymerization but is far to be comparable to reaction [5] reducing crosslinking.

Figure 4 shows the effect of the allylic halides on the intrinsic viscosity of the polymer. We observe that the effect of allylic halides on the molecular weight appears rather complicated. In fact, the [η] value increases at low halide concentrations and then decreases while halide concentration reachs high. According to the chain transfer proposition (see equation [5]), the molecular weight would be reduced by the addition of halides, as shown in the polymerizations of PD in the presence of the tertiary halides (7). However, the result illustrated by Figure 4 does not fall into this consideration. We suspect that the effect of the allylic halides on the polymer molecular weight could not be described only by equation [5]. There are other factors responsable for the augmentation of the molecular weight. We suppose that this might be attributed to the possible enhancement effect of the allylic halides for $AlCl_3$ by complexation. Adimittedly, to our knowledge it is not yet possible to fully elucidate this result at present.

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