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Cationic polymerization of 1,3-pentadiene in the presence of arenes

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Summary

The cationic polymerizations of 1,3-pentadiene initiated by $AlCl_3$ in n-hexane at 30℃ have been carried out in the presence of various arenes, i.e., benzene, toluene, p-xylene, o-xylene, m-xylene and mesitylene. The presence of all these arenes have reduced to different extents the formation of crosslinked products. Namely, the crosslinking reaction, a major side-reaction during the cationic polymerization of 1,3-pentadiene, has been suppressed by adding the aromatic compounds. The results showed that a chain transfer to arene takes place and this transfer process hinders the generation of the crosslinked polymer. IR and ^1H NMR evidences have confirmed the existence of the corresponding aryl groups in the resulting polymers.

Introduction

The cationic polymerizations of 1,3-pentadiene (PD) have been initiated by various Lewis acids(1-3). In many circumstances, insoluble crosslinked polymers were readily generated during the polymerization process. $(TfO)_3Al$-induced PD polymerization(4) could avoid the formation of crosslinked products but gave the polymer having a relatively low molecular weight. In fact, crosslinking reaction is a major side-reaction frequently occuring during the cationic polymerization of conjugated dienes(5).

As it has been known that the formation of crosslinked products could be hindered by using some aromatic solvents for the cationic polymerization of PD, we became interested in the function of aromatic compounds on this polymerization.

We report briefly in the present work the results of our preliminary study on the effect of various arenes on the PD polymerization initiated by $AlCl_3$ in n-hexane at 30℃.

Experimental

1 Materials

1,3-Pentadiene from Fluka was dried with CaH_2 and distillated. n-Hexane and all the arenes were also distillated over CaH_2. $AlCl_3$ was purified by sublimation in vacuum.

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2 Polymerization

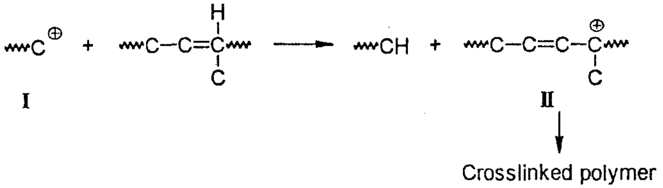
$AlCl_3$ and the solvent were introduced in a three-neck-flask equiped with a stirer, a reflux condenser and a nitrogen inlet. The arene was added by syringe and the monomer was finally introduced at the given temperature also by syringe. The polymerization was quenched by methanol-containing n-hexane in a given time. The reaction solution was filtered to obtain the insoluble crosslinked product. After washing with water the resulting solution was evaporated under reduced pressure to recover the soluble polymer.

3 Measurements

IR and ^1H NMR spectra were measured with a Microlab MX620 spectrometer and a Virian FT-80A spectrometer, respectively. Intrinsic viscosity was determined with an Ubbelohde viscometer in cyclohexane at 25℃.

Results and discussion

In the cationic polymerization of conjugated dienes, crosslinking reaction frequently takes place due to the formation of a carbocation through a hydride transfer at the α-position of the double bond remaining in polymer chains(5). For example, in the cationic polmerization of PD:



$$\sim\sim C^{\oplus} + \sim\sim C{-}C{=}\overset{H}{\underset{C}{C}}\sim\sim \longrightarrow \sim\sim CH + \sim\sim C{-}C{=}C{-}\overset{\oplus}{\underset{C}{C}}\sim\sim \quad (1)$$

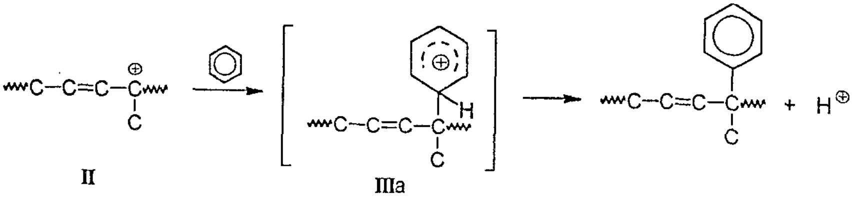
In the PD polymerization initiated by $AlCl_3$ in n-hexane at 30℃, crosslinked polymers were readily generated. However, we discovered that the crosslinking reaction could be essentially reduced by adding aromatic compounds. Table 1 gives the results of the polymerizations in the absence and presence of various arenes:

Table 1 Cationic polymerizations of PD in the absence and presence of arenes[a]

Run	Arene	Conversion (%)			[η] (dl/g)	Unsaturation loss (%)[b]
		Soluble polymer	Crosslinked product	Total		
1	None	41.0	31.1	72.1	0.075	68.6
2	Benzene	45.9	30.8	76.7	0.081	76.5
3	Toluene	75.4	4.2	79.6	0.073	66.6
4	p-Xylene	65.5	3.3	68.8	0.082	60.0
5	o-Xylene	68.8	1.0	69.8	0.079	73.8
6	m-Xylene	72.1	trace	72.1	0.088	55.9
7	Mesitylene	72.1	6.3	78.4	0.070	59.7

[a] [PD] = 2mol/l; [$AlCl_3$] = 2×10^{-2} mol/l; Solvent: n-hexane; [Arene]/[$AlCl_3$] = 10; Reaction temperature: 30℃; Time: 4h. [b] Calculated from ^1H NMR spectra of the polymers.

As shown in Table 1, the presence of these aromatic compounds has reduced or eliminated the formation of the crosslinked polymers to different extents. As the carbocation during a cationic polymerization can undergo a chain transfer to a aromatic group (6), we suggest that the presence of aromatic compounds in the present polymerization could react with the carbocation II generated in equation (1) through a chain transfer reaction, and the crosslinking process is therefore hindered. In the presence of benzene, for example:



(2)

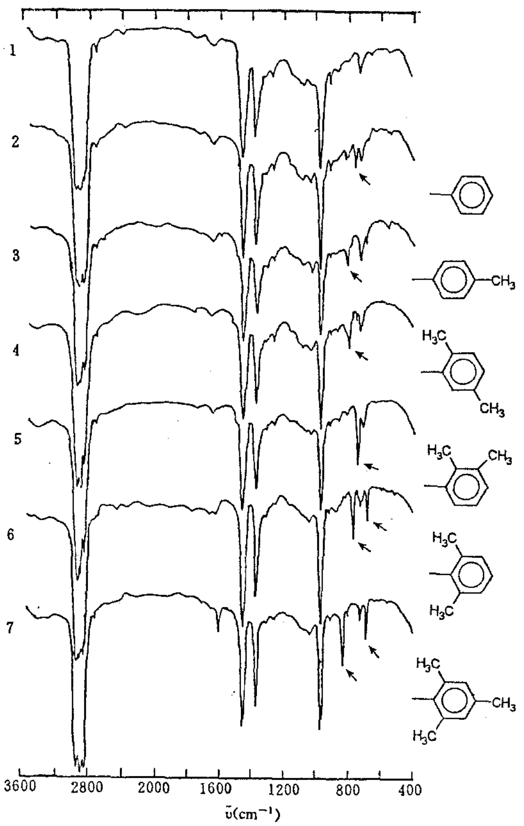


Figure 1 IR spectra of the polymers prepared in n-hexane at 30℃ in absence and in the presence of various arenes. Reaction conditions in Table 1. 1-Run 1; 2-Run 2; 3-Run 3; 4-Run 4; 5-Run 5; 6-Run 6; 7-Run 7.

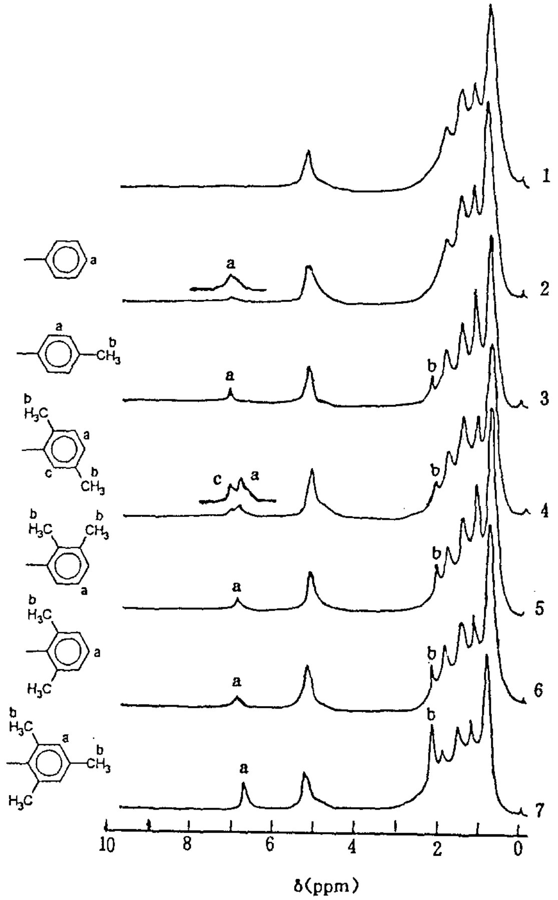
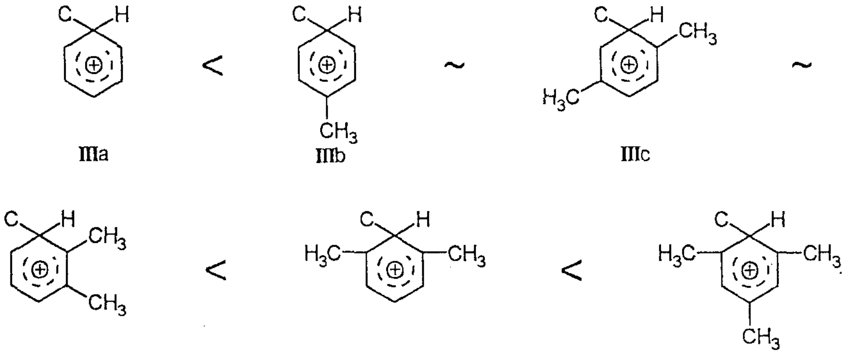


Figure 2 ^{1}H NMR spectra of the polymers prepared in n-hexane at 30℃ in absence and in the presence of various arenes. Reaction conditions in Table 1. 1-Run 1; 2-Run 2; 3-Run 3; 4-Run 4; 5-Run 5; 6-Run 6; 7-Run 7.

A direct evidence for the above reaction has been given by IR and ^{1}H NMR spectra of the polymers. As shown by IR spectra in Figure 1, all these corresponding aryl groups exist in the polymers. Among them the signal of phenyl group in the polymer of Run 2 in Table 1 appears the most weak, in accordance with the lowest reactivity of benzene toward carbocation II. The ^{1}H NMR spectra of the polymers have been shown in Figure 2. The existence of each aromatic groups for these arenes have been again found in these polymers.

In the chain transfer reaction illustrated in equation (2), theoretically, the reactivities of these arenes should give an order corresponding to the stabilities of their transition states III. Based on the structures of the aromatic groups measured by IR and NMR, we could obtain a stability order for these transition states:



IIIa IIIb IIIc

IIId IIIe IIIf

This order seems to conform to the reactivity order of the aromatic compounds shown in Table 1 with an unique exception for mesitylene. In fact, transition state **IIIf** resulted from mesitylene should be the most stable among all these six. However, mesitylene seems to act as a less strong crosslinking suppressor than xylenes. Perhaps we could attribute this phenomenon to the bulky hindrance of the reaction between mesitylene and a tertiary carbocation.

As the cationic polymerization of PD was always accompanied by cyclization, another side-reaction, unsaturation loss has been used to characterize the content of cyclic structures of cationically polymerized polypentadiene (4). As shown in Table 1, the arenes have not influenced the unsaturation loss of resulting polymers, which means that the cyclization reaction could not been suppressed by adding the arenes .

Obviously, in addition to carbocation **II**, the growing carbocation (**I**) can also undergo a similar transfer reaction with arenes and this chain-breaking transfer will result in the decrease of the molecular weight of the polymer. Table 1 gives the intrinsic viscosity values of the polymers. We found that the presence of the arenes has also a limited effect on the molecular wight of the polymers. This result shows that the chain transfer of carbocation **I** to arenes is much less significant compared with transfer reaction (2) in the present reaction conditions.

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