Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Peng, Y. X. , Deng, Y. G. , Liu, J. L. , Dai, H. S. and Cun, L. F.(1996) 'Effect of Organic Halides on Cationic Polymerization of Isoprene', Journal of Macromolecular Science, Part A, 33: 1, 133 — 139

To link to this Article: DOI: 10.1080/10601329608020367

URL: http://dx.doi.org/10.1080/10601329608020367

MACROMOLECULAR REPORTS, A33(SUPPL. 2), 133-139 (1996)

EFFECT OF ORGANIC HALIDES ON CATIONIC POLYMERIZATION OF ISOPRENE

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ABSTRACT

The cationic polymerizations of isoprene initiated by $AlCl_3$ in various solvents were carried out in the presence of organic halides, i.e., tert-butyl chloride, 3-chloro-1-butene, and benzyl chloride. The presence of the halides can strongly suppress the crosslinking reaction presenting during the polymerization. The halides also exert an effect on the cyclization process in this polymerization system. Investigations on the microstructure of the polymer show that the content of cyclic segments of polymer chains is increased by the addition of the halides. In addition, the influences of halides on polymer yield and molecular weight are also discussed.

INTRODUCTION

The cationic copolymerization of isoprene (IP) with isobutylene, the most significant industrial cationic polymerization process, has long been well demonstrated [1]. However, the cationic homopolymerization of isoprene (IP) is not attractive due to its ill-defined polymer structure which is always a mixture of

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linear, cyclic, branched and crosslinked segments [2]. Polymerizations of IP initiated by various Friedel-Crafts acids [3,4] produce usually both insoluble (crosslinked) product and soluble polymer consisting of linear and cyclic sigments. The protic acid-induced polymerization [5] can avoid the formation of crosslinked products but generates only highly cyclized oligomers. In fact, crosslinking and cyclization are two characteristic side reaction which seem difficult to avoid during the cationic polymerization of conjugated dienes such as 1,3-butadiene, isoprene and 1,3-pentadiene.

We have recently discovered that some alkyl halides exert a strong reduction effect on crosslinking during the cationic polymerization of 1,3-pentadiene [6]. The present work describes the reduction effect of tert-butyl chloride (t-BuCl), 3-chloro-1-butene (ClBu) and benzyl chloride (BenCl) on the crosslinking reaction during the IP polymerization initiated by $AlCl_3$.

EXPERIMENTAL

Materials

Isoprene (IP) from Fluka was distilled over CaH_2. The solvents were also distilled over CaH_2. $AlCl_3$ was purified by sublimation in vacuum. t-BuCl, ClBu, and BenCl from Fluka were used as received.

Polymerization

$AlCl_3$ was introduced in a three-necked-reactor in dry nitrogen atmosphere. The solvent and halide were added and then the polymerization was achieved by introduction of IP 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 and 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.

Table 1. Effect of the halides on the polymerization in toluene at 30°C[a]

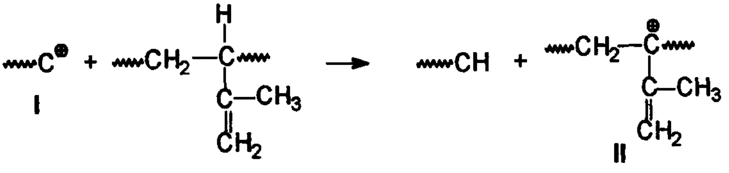
Run	Halide	Polymer yield (%)			[η] (dl/g)	Microstructure[b] (%)		
		Soluble polymer	Cross-linked	Total yield		linear		Cyclic
						1,4-unit	3,4-unit	
1	None	64	26	90	0.063	75	5	20
2	t-BuCl	~100	0	~100	0.024	35	5	60
3	ClBu	90	0	90	0.042	0	0	100
4	BenCl	87.5	0	87.5	0.019	45	5	50

[a] [IP]=1.5mol/L, $[AlCl_3]=3\times10^{-2}$mol/L, $[Halide]/[AlCl_3]=5$, Reaction time: 4h.
[b] Calculated from ^1H NMR spectra of the polymer [7].

RESULTS AND DISCUSSION

Table 1 summarizes the results of polymerizations of IP initiated by $AlCl_3$ in toluene at 30°C in the absence and presence of t-BuCl, ClBu and BenCl. It is shown that the formation of crosslinked polymers in the polymerization of IP is completely eliminated by the addition of the three halides, indicating that these halides exert strong crosslinking-reduction effects in the present conditions. Table 1 shows also that the intrinsic viscosity of the polymer decreases with the addition of the chlorides.

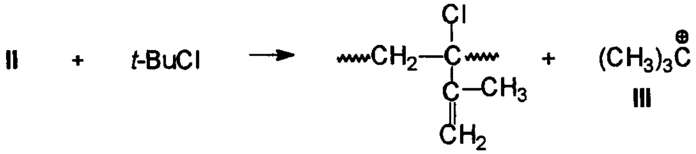
It has been known that during the cationic polymerization of IP the crosslinking reaction is readily induced by the macromolecular cation (II) which is formed through the intermolecular hydride shift between the propagating carbocation (I) and the polymer chain containing 3,4-units [1]. Schematically, these reactions can be illustrated as follows:



$$\underset{\mathrm{I}}{\sim\!C^{\oplus}} + \sim\!CH_2-\overset{H}{\underset{\underset{CH_2}{\overset{\|}{C}-CH_3}}{C}}\!\sim \longrightarrow \sim\!CH + \underset{\mathrm{II}}{\sim\!CH_2-\overset{\oplus}{\underset{\underset{CH_2}{\overset{\|}{C}-CH_3}}{C}}\!\sim} \qquad (1)$$

$$\mathrm{II} + \mathrm{IP} \longrightarrow \text{Branched and crosslinked polymers} \qquad (2)$$

To explain the crosslinking-reduction effect of the halides, we propose a chain transfer reaction of cation **II** leading to crosslinked structures to the added halides. For example, in the presence of t-BuCl,



$$\mathbf{II} + t\text{-BuCl} \longrightarrow \sim\!CH_2-\overset{Cl}{\underset{\underset{CH_2}{\parallel}}{C}}\!\sim \ (C-CH_3) + \underset{\mathbf{III}}{(CH_3)_3\overset{\oplus}{C}} \qquad (3)$$

The above chain transfer is a competitive reaction with crosslinking reaction (2) and It can therefore substantially suppress the crosslinking process. As the newly formed cation **III** has a comparable reactivity to **II** and is able to sustain the propagation, hence the addition of the halides does not stop the kinetic chain and exert a quite limited on polymer yield, as shown in Table 1.

Obviously, in addition to reaction (3), the chain growing carbocation (cation **I**) can also undergo a similar chain transfer to halides, which will results in the depression of molecular weights:

$$\mathbf{I} + t\text{-BuCl} \longrightarrow \sim\!CCl + \mathbf{III} \qquad (4)$$

Therefore, the overall effect of the halides in the cationic polymerization of IP is described by both reactions (3) and (4). The consenquence of the former is the reduction or elimination of crosslinking reaction while the latter is responsable for the decrease of the molecular weight.

In order to understand the influence of the halides on the microstructure of polymer chains, we obtained ^{1}H NMR spectra of the polymers shown in Figure 1. On the spectrum of the polymer prepared in the absence of halides, we observe in the region of unsaturated protons three peaks. The signal at 5.25ppm is attributed to unsaturated protons of cyclic structures, while the peaks at 5.05ppm and 4.65ppm are contributed by unsatruated protons of linear 1,4- and 3,4-units respectively. In the presence of halides, the signal at 5.25ppm shows a higher while the peaks at 5.05ppm and 4.65ppm present . We conclude that the cyclization reaction during the polymerization is enhanced by the addition of

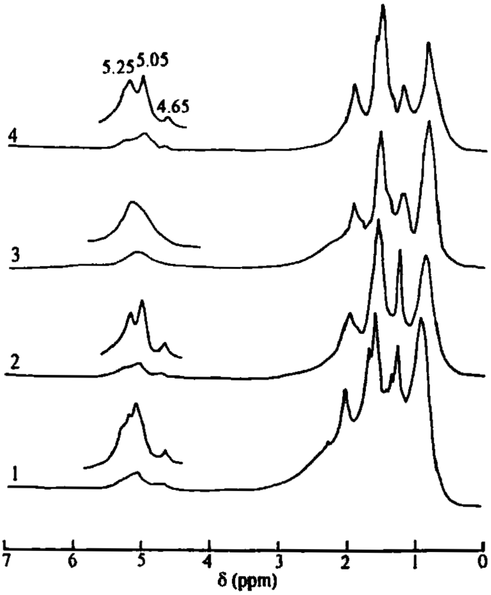


Figure 1. ^{1}H NMR spectra of the polymers prepared in the absence (1) and presence of *t*-BuCl (2), ClBu (3), and BenCl (4).

halides. Particularly, the polymer prepared in the presence of ClBu (spectrum 3) shows a totally cyclized structure.

With the integration intensities of these three signals, we calculated the microstructure of the polymer chain [7] which are summarized in Table 1. It is shown that all the three halides have an enhancing effect on cyclization. As a result, the microstructure of polymer chains has a relatively high cyclic fraction in the presence of halides. It is known that the cyclization in the cationic polymerization of IP is a rather complicated process [8]. To our knowledge it is not yet possible to elucidate the cyclization enhancing effect of the halides in the present polymerization system.

The effects of halides on the polymerizations in n-hexane and methylene chlorides at 30°C are presented in Table 2. We observe that the halides fail to show any

Table 2. Effect of halides on polymerizations in n-hexane and CH_2Cl_2 at 30°C[a]

Run	Solvent	Halide	Polymer yield (%)			[η] (dl/g)	Microstructure[b] (%)		
			Soluble polymer	Cross-linked	Total yield		linear		Cyclic
							1,4-unit	3,4-unit	
5	n-hexane	None	3	4	7	-	55	10	35
6	n-hexane	t-BuCl	27	40	67	-	40	5	40
7	n-hexane	ClBu	44	52	96	0.017	35	5	60
8	n-hexane	BenCl	30	32	62	-	45	5	50
9	CH_2Cl_2	None	76	8.5	84.5	-	10	5	85
10	CH_2Cl_2	t-BuCl	54	2.5	56.5	0.050	15	5	80
11	CH_2Cl_2	ClBu	90	1.5	91.5	0.098	25	5	70
12	CH_2Cl_2	BenCl	90	8	98	0.051	0	0	100

[a] [IP]=1.5mol/L, $[AlCl_3]=3\times10^{-2}$mol/L, [Halide]/$[AlCl_3]$= 5, Reaction time: 4h.
[b] Calculated from ^{1}H NMR spectra of the polymer [7].

Table 3. Effects of halides on polymerizations in toluene and n-hexane at 0°C[a]

Run	Solvent	Halide	Polymer yield (%)		
			Soluble polymer	Cross-linked	Total yield
13	toluene	None	21	23	44
14	toluene	t-BuCl	95	0	95
15	toluene	ClBu	97	0	97
16	toluene	BenCl	90	0	90
17	n-hexane	None	4	1.5	4.5
18	n-hexane	t-BuCl	14	13	27
19	n-hexane	ClBu	15	85	100
20	n-hexane	BenCl	25	17	42

[a] [IP]=1.5mol/L, $[AlCl_3]=3\times10^{-2}$mol/L, [Halide]/$[AlCl_3]$= 5, Reaction time: 4h.
[b] Calculated from ^{1}H NMR spectra of the polymer [7].

crosslinking reducing effect in n-hexane. The cyclization enhancing effect also becomes much weaker. However, we found that the halides give a strong enhancing effect on the total yield. We conclude that in this medium the halides are likely to act as initiator in conjunction with $AlCl_3$, but not as chain transfer agent. Therefore, the halides, which have been known as "inifer"[9], could exert different effects in different reaction conditions. Table 2 shows also that in methylene chlorides the halide does not show crosslinking reducing effect nor cyclization enhancing effect.

We have also carried out the polymerizations in toluene and n-hexane at 0°C (Table 3) to obtain the influence of temperature on the effects of halides. It is shown that the crosslinking reducing effect of halides in toluene remains rather strong at 0°C. All the polymerizations in the presence of halides are free of crosslinked polymers. Table 3 shows also that the enhancing effect of halides on polymer yield in n-hexane becomes weaker at 0°C for t-BuCl and BenCl. But 3-chloro-1-butene gives always a strong effect, which indicates that the $ClBu/AlCl_3$ combination is an effective initiating system for the polymerization of IP in the present conditions.

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