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How does Cross-Linking Effect the Thermal Stability of Polyisoprene

Qiang Yao
Marquette University

Charles A. Wilkie
Marquette University, charles.wilkie@marquette.edu

Marquette University

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How does cross-linking affect the thermal stability of polyisoprene?

Qiang Yao

Department of Chemistry, Marquette University, PO Box 1881, Milwaukee, WI 53201, USA

Charles A. Wilkie

Department of Chemistry, Marquette University, PO Box 1881, Milwaukee, WI 53201, USA

Abstract

[Polyisoprene](#) can be cross-linked by an initial [lithiation](#) followed by reaction with both monochloro compounds and dichloro compounds. The monochloro compounds effect [crosslinking](#) through a lithium-chlorine exchange route while the use of dichloro compounds links the PIP chains with the spacer between the two [chlorine atoms](#). A significant amount of char is produced from compounds which have been cross-linked with aromatic dihalides while aliphatic dihalides do not produce significant char.

Keywords

Polyisoprene, Cross-linking, Thermogravimetric analysis, Char, Lithiation

1. Introduction

Cross-linked polymers remain an area of significant interest for enhancing the flame retardancy of polymeric materials, due to the formation of a network which is expected to increase the difficulty of eliminating small molecules. In principle, chemical cross-linking reduces the molecular mobility and increases the number of bonds which must be broken in order for a material to exhibit mass loss. There have been numerous papers discussing the structures and thermal stability of polymers. Arnold [1] reviewed the stability of high-temperature polymers, while Van Krevelen [2] correlated polymer structures with char yield and flame resistance and found that an increase in aromaticity yields a larger amount of char and decreases the flammability. These works were primarily concerned with linear polymers; there have been only a small amount of works in which the influence of cross-links and the cross-linking structure on thermal stability has been investigated.

In recent work from this, and other, laboratories, polyamides [3], [4] polybutadiene and its copolymers and related polymers [5], [6], [7], [8] and methacrylate and styrenes [9] have been cross-linked. In the majority of cases, no improvement in the thermal stability of the polymer has been noted from the cross-linking reaction. Only with copolymers of styrene with divinylbenzene has an enhanced thermal stability been noted. Based upon this work, it was felt that the type of cross-link was more important than the number of cross-links. An aromatic cross-link appears to offer enhanced thermal stability while an aliphatic material does not.

Polydienes, such as polybutadiene and polyisoprene, have been previously studied in these laboratories and are of interest as models to examine the effects of cross-linking on thermal stability. The metalation of diene polymers has been reported by several research groups. Minoura and co-workers [10] found that the metalation of diene polymers with *n*-butyllithium in *n*-heptane proceeds in the presence of *N, N, N', N'*-tetramethylethylenediamine (TMEDA) with some degree of chain scission. Falk et al. [11] have reported the metalation of diene polymers by *sec*-butyllithium with TMEDA and found that the use of *sec*-butyllithium/FMEDA eliminates backbone chain degradation at room temperature. Metallated diene polymers are well known to undergo reactions such as graft copolymerisation [12], [13], [14] and coupling reactions with halogen-containing compounds [15]. The coupling reaction between metallated diene polymers with di-halogen compounds allows one to cross-link the diene polymers and obtain a variety of moieties as the cross-link. This enables the investigation of the effect of the cross-linking structure on the thermal stability.

In this paper, we report the coupling reaction between the metallated polyisoprene with (di)halogen compounds with different structures and examine the thermal stability of cross-linked polyisoprene and discuss the influence of the cross-link structure on the char yield.

2. Experimental

2.1. Materials

All materials are purchased from Aldrich Chemical Company and used as received; this includes *cis*-polyisoprene, *sec*-butyllithium (1.3 M in cyclohexane), anhydrous 1-chlorobutane, 1-chlorobenzene, *n*-heptane and cyclohexane. All chemicals were of reagent grade or better.

2.2. Instrumentation

¹H and ¹³C NMR spectra were measured using a GE 300 MHz spectrometer with CDC₁₃ as solvent. ²H NMR spectra were recorded on the same spectrometer with CCl₄ as a solvent. FTIR spectra were recorded on a Nicolet Magna-IR 560 infrared spectrometer at 4 cm⁻¹ resolution as thin films or KBr pellets. Thermogravimetric analyses were performed on an Omnitherm 1000 unit at a rate of 20°C/mm under flowing nitrogen.

2.3. Lithiation of squalene and hydrolysis

In a 100 ml flask, equipped with a condenser, nitrogen sparger and a magnetic stirrer, 4.113 g squalene (10.0 mmol), 46 ml of 1.3 M *sec*-butyllithium (0.06 mmol) and 9 ml TMEDA (0.06 mmol) were combined. The solution was allowed to react for 1 h and exhibited an intense reddish color. The reaction was terminated by adding excess methyl alcohol-*d* to the mixture. The mixture was extracted by water three times and dried in vacuum oven at room temperature for 1 week.

2.4. Lithiation of polyisoprene

A 100 ml flask, equipped with a condenser, nitrogen sparger and a magnetic stirrer, was charged with a predetermined amount of *n*-heptane and 0.44 g polyisoprene (6.5 mmol of repeat units); the mixture was kept at 60°C until the polyisoprene was completely dissolved. After dissolution was complete, the mixture was cooled to room temperature and a predetermined (and variable) amount of TMEDA/*sec*-butyllithium (1:1) was added drop-wise to the mixture; the total volume of solution was 50 ml. The solution was allowed to react for 1 h and exhibited a reddish coloration. At large amounts of TMEDA/*sec*-butyllithium ($[\text{BuLi}]/[\text{PIP}] > 1$), gelation occurs. Gelation also occurs if the stirring stops. Lithiated polyisoprenes are indicated as PIP-Li.

2.5. Hydrolysis of lithiated polyisoprene

After lithiation was deemed complete, excess methanol was added to the solution. The reddish color disappeared and two layers were formed rather than a precipitate. The addition of a small amount of *n*-propanol results in the formation of a large amount of precipitate. The polymer was purified using a mixture of tetrahydrofuran (THF)/methanol as the solvent/non-solvent. The hydrolysis product of lithiated polyisoprene is represented as PIP-H.

2.6. Coupling reactions of lithiated polyisoprene with dichloro-compounds

A predetermined (and variable) amount of di-halogen compound, in all cases the ratio of the di-halogen compound to *sec*-butyllithium was 0.45, was added dropwise after the completion of the lithiation reaction. In the case of 1,2-dichloroethane (DCE) and 1,4-dichlorobutane (DCB) as the cross-linking reagents, immediate gelation occurs. A very dark chocolate solution was observed if 1,4-dichlorobenzene (DCPh) was used. For α , α' -dichloro-*p*-xylene (DCAr), anhydrous cyclohexane was used in place of *n*-heptane in order to increase the solubility of α , α' -dichloro-*p*-xylene. In one trial, 5ml THF was added to dissolve α , α' -dichloro-*p*-xylene and gel formation was observed. All the coupling reactions were allowed to continue for 1 h and were terminated by the addition of excess methanol/water containing 1% HCl. The final products were colorless, except for those obtained by DCAr which appeared yellow. All the cross-linked samples were obtained by permitting the solvent to evaporate in the hood overnight and then drying in the vacuum oven at room temperature for 24 h; the dried samples were then extracted with THF for 24 h and the swelling ratios were determined [16], [17]. The swelling ratio is obtained from the mass of solvent-swollen polymer to that of solvent-free polymer. The final cross-linked PIPs by dichloro-compounds are represented by PIP-R-PIP.

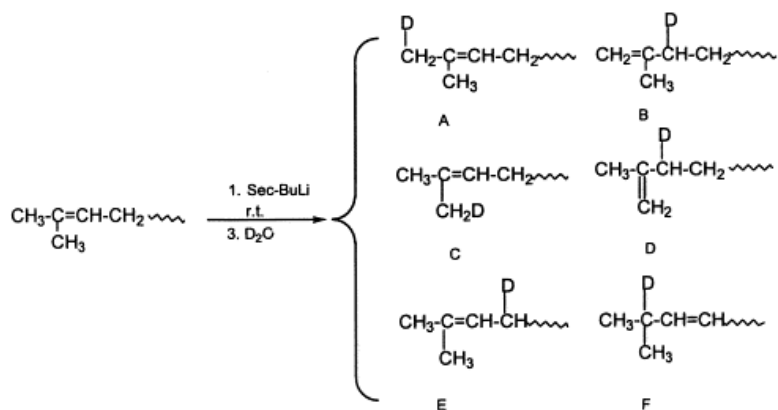
2.7. Coupling reaction of lithiated polyisoprene with monochloro-compounds

A predetermined amount of monochloro-compounds, the ratio of monochloro compound to *sec*-butyllithium was 0.9, was added drop-wise after the completion of the lithiation reaction. For benzyl chloride (MBC) and 4-methylbenzyl chloride (MMBC), immediate gelation was observed; a rust colored solution was observed for chlorobenzene (MCBn) and a viscous yellow solution was obtained for both 1-chlorobutane (MCB) and 1-chlorohexane (MCH). After 1 h, the reaction was terminated by the addition of excess methanol and the precipitated polymers were dried and extracted by THF according to the above procedure. The final cross-linked PIPs from monochloro-compounds are represented by PIP-PIP.

3. Results and discussion

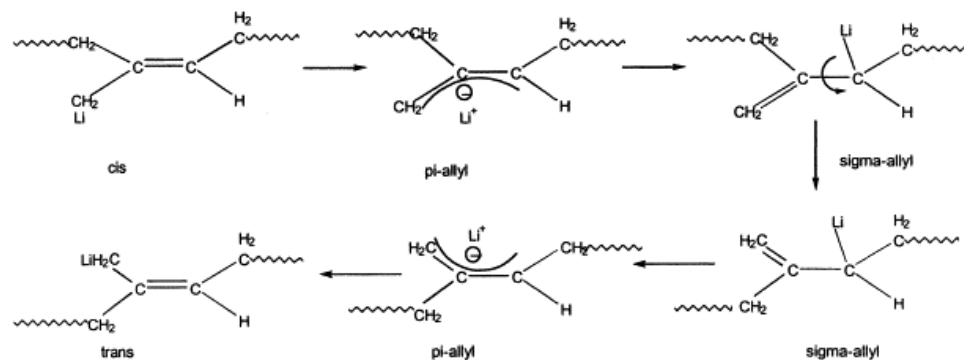
3.1. Lithiation site

The metallation of polydiene has been reported and applied to obtain graft copolymers by several research groups, unfortunately few details about the site of metallation have been provided. Minoura and co-workers [10] analyzed the infrared spectra of the hydrolysis products of lithiated squalene, the model compound for polydiene, and found that they were the same as that of the original squalene and that unsaturation showed little reduction and the molecular weight was unchanged. Because carbonation of lithiated squalene showed the presence of the carboxylic group, they concluded that the lithiation occurs by the exchange of lithium with the allylic hydrogen of squalene. Their results were confirmed in this laboratory by both ^1H and ^2H NMR spectra. Three broad peaks are observed, at $\delta = 2.14$, 1.85 and 1.79, in the ^2H spectrum and these were assigned to the α -allylic deuterium, suggesting that the exchange reaction took place between lithium and the allylic hydrogen (Scheme 1). Although the formation of π -allyl has several resonance structures and would give more deuterated products, no other appreciable peaks were detected in ^2H spectrum, probably due to either unstable allylic species or peak overlaps. New, broad peaks at $\delta = 4.73$ in the ^1H spectrum were observed and assigned to the hydrogen of vinylidene [18], a group resulting from the rearrangement of π -allyl to σ -allyl.



Scheme 1. [Lithiation](#) and [hydrolysis](#) of [squalene](#) (only a portion of the squalene structure is shown).

This new NMR peak is also observed for polyisoprene. The peak increases as amount of *sec*-butyllithium is increased, suggesting an increased extent of lithiation. Another new peak at $\delta = 1.61$ in the ^1H spectrum, absent in the original polyisoprene, indicates the presence of *trans* 1,4-polyisoprene [7], suggesting *cis* to *trans* isomerization. This isomerization may be accomplished by the rearrangement of π -allyl to the σ -allyl followed by bond rotation [19] and is shown in Scheme 2. The presence of vinylidene and isomerization indicates that the lithiation site of polyisoprene occurs in the allylic hydrogen position, as observed for squalene.



Scheme 2. [Isomerization](#) of lithiated [polyisoprene](#).

The ^{13}C spectrum of the hydrolysis product of the lithiated polyisoprene is consistent with *cis-trans* isomerization and the presence of vinylidene. Distinct absorptions were observed at $\delta=135.64$ and 124.86 and were assigned to the C2 and C3 in *trans* 1,4 polyisoprene, respectively, the resonance for the C1, C4 and C5 carbons were found at $\delta=40.70$, 27.29 and 16.64 , respectively, and were very close to the published data [20], [21]. The C2 and C5 resonances of vinylidene units are observed at $\delta=150.08$ and 109.45 , respectively, no corresponding peaks are found in the original polyisoprene. There are other small peaks at $\delta=135.7-136.1$, $124.5-126.0$, $40.0-40.5$, $36.5-37.5$, $32.0-32.8$, 26.8 which may arise from the various rearrangement units and the linkage of different structure units. Because of extreme complication of these structures, no assignment was made.

The FTIR spectrum of the hydrolysis product of the lithiated polyisoprene is also in accord with the rearrangement. In contrast to the results obtained by Minura [12], in this study the infrared spectrum of the hydrolysis product is different from that of the starting material; a new peak at 1640 cm^{-1} is observed, which is assigned to the double bond stretching vibration of vinylidene. Based on the ^2H , ^1H , ^{13}C and FTIR spectra, it can be concluded that lithiation occurs in polyisoprene by the exchange of lithium and allylic hydrogen.

3.2. Cross-linked PIP by monochlorinated compounds

The coupling reaction between lithiated compounds and chloro-compounds is usually accompanied by side reactions such as lithium-chloride exchange [22], [23], [24] and radical reactions [25], [26] so cross-linked PIP can be obtained by treating lithiated PIP with monochlorinated compounds. Because no additional structures were incorporated into the cross-linking bridge, this PIP-PIP is self cross-linked.

When chlorinated compounds were added to the lithiated PIP solution, cross-linked products were observed. If *sec*-BuLi was added to the chlorinated-compounds-containing PIP solution, no cross-linking is observed. If a radical mechanism dominates the coupling reaction between organolithium reagents and chloro-compounds, radicals should be produced irrespective of the order of addition. In the latter case, the hypothetically produced *sec*-Bu radicals would abstract the allylic hydrogen in the PIP, and, therefore, PIP macroradicals and cross-linked products should be formed. The absence of cross-linked products in the latter case suggests that radical-coupling mechanism be not responsible for the formation of cross-linked products in the first case but rather lithium-chloride exchange route be considered to be the major pathway of cross-linking under these conditions [27].

The swelling ratios and thermogravimetric analysis are listed in Table 1, and the TGA curves are shown in Fig. 1, for PIP-PIP cross-linked by various monochlorinated compounds. It is notable that only a major single step is observed in the thermal degradation. The values recorded in Table 1 include the swelling ratio, SR%, the onset temperature of 3% degradation, T3%, and of 50% degradation, T50%, the temperature for the mid-point of the degradation step, obtained from the derivative, T_{max} , and the maximum rate of weight loss, r_{max} , also from the derivative, and the char yield at 500°C .

Table 1. Results of [thermogravimetry](#) analysis of PIP-H and various simply cross-linked PIP

Sample	[BuLi]	SR% (± 100)	T3% ($\pm 2^\circ\text{C}$)	T50% ($\pm 1^\circ\text{C}$)	T_{max} ($\pm 1^\circ\text{C}$)	r_{max} ($\pm 0.5\%/ \text{min}$)	Char at 500°C ($\pm 1\%$)
PIP-H ^a	0.52	–	348	408	403	–30.1	2.3
	0.13	–	351	403	399	–33.1	1.0
	0.065	–	354	403	401	–33.9	1.8
	0	–	356	402	400	–37.0	1.0
PIP-MCH ^b	0.13	Very high	345	403	401	–32.3	2.5
	0.033	5100	350	402	400	–33.7	2.1
PIP-MCB ^c	0.13	Very high	349	403	400	–31.1	2.0

	0.065	5100	348	403	400	-31.0	2.3
	0.033	5100	352	403	399	-32.8	2.0
	0.013	4200	348	402	401	-34.50	2.4
PIP-MMBC ^d	0.13	3200	318	405	402	-28.2	1.9
PIP-MBC ^e	0.033	3800	300	402	400	-32.9	2.3
PIP-MCBn ^f	0.033	8400	334	402	400	-32.1	2.0

- a Hydrolysis product of lithiated polyisoprene.
- b Crosslinked PIP, using 1-chlorohexane.
- c Crosslinked PIP, using 1-chlorobutane.
- d Crosslinked PIP, using 4-methylbenzyl chloride.
- e Crosslinked PIP, using benzyl chloride.
- f Crosslinked PIP, using chlorobenzene.

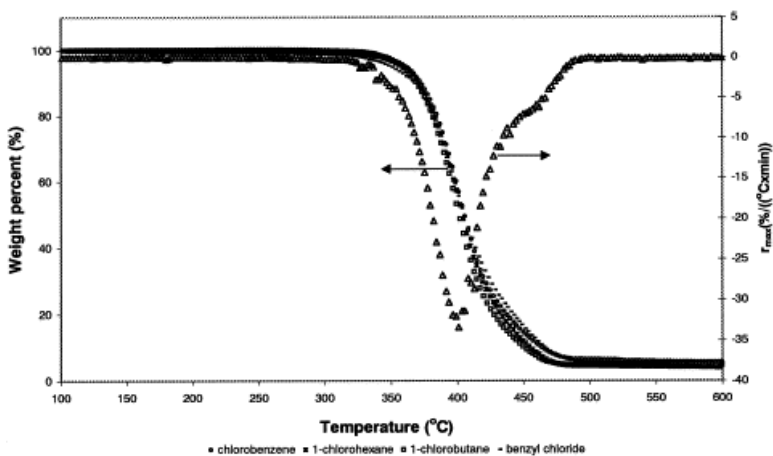


Fig. 1. [Thermogravimetric analysis](#) of PIP-PIP cross-linked by various monochloro-compounds at $[\text{BuLi}] = 0.033$ mol/l at $20^\circ\text{C}/\text{mm}$ under N_2 .

Falk et al [4] reported that no backbone chain degradation of PIP took place if *sec*-BuLi/TMEDA was used. The TGA curves of the hydrolysis products of lithiated PIP show a decreased thermal stability, as measured by the onset of the degradation, T3%, as the amount of *sec*-butyllithium increases. The highly lithiated PIP-H also has a low value of the maximum rate of change, r_{max} and a high temperature for the mid-point of the degradation step, T50%. These changes may be indications that *sec*-BuLi has some effect on the thermal stability of PIP and could be due to the structure change of PIP such as isomerization during lithiation.

All PIP-PIP samples have high swelling ratios and, therefore, their cross-linking density is rather low. Among the PIP-PIP materials, the samples which were reacted with benzyl chloride and 4-methylbenzyl chloride have the lowest swelling ratios while 1-chlorobutane and 1-chlorohexane have intermediate values and chlorobenzene has the highest swelling ratio. This extent of cross-linking must be a reflection of the rate of Li-Cl exchange and a competition between different exchange reactions. Benzyl chloride and 4-methylbenzyl chloride are the most active toward exchange between chloride and PIP-Li so PIP-Cl is easily produced and a relatively high cross-link density can be obtained. Chlorobenzene is readily exchanged to give the corresponding lithium compounds by *sec*-BuLi [28] so less exchange can occur between chlorobenzene and PIP-Li and the swelling ratio is quite high.

When the concentration of *sec*-BuLi was 0.13 M or higher, no gelation was observed for the reaction of lithiated PIP with 1-chlorohexane and 1-chlorobutane, because the elimination of HCl from the chloroalkane effectively competes with the coupling reaction. When the concentration of the lithium reagent was lower than 0.13 M, gelation was always observed.

The TGA curves are similar for all PIP-PIPs and overlap. T_{\max} , T50% and r_{\max} are independent of the cross-linking reagents, and the amount of char that is produced is comparable to that from virgin PIP. T_{\max} and T50% are close to each other for all samples; this relationship is consistent with the results of Van Krevelen for linear polymers [2]. Moreover, these simply cross-linked PIPs show only a single major degradation step, coincident with that for PIP-H treated with the same amount of *sec*-butyllithium. These results can be attributed to either the very high swelling ratios, i.e. low degrees of cross-linking, or the simple cross-linking process or both. The high swelling ratios indicate a low extent of cross-linking, and therefore no significant improvement is expected in thermal stability and char yield. Since the simple cross-linking process does not introduce any new features in the polymer, no changes in the TGA curve may be expected.

3.3. The FTIR spectra of PIP cross-linked by dichloro-compounds.

The PIP-R-PIPs are examined by the FTIR spectroscopy in order to ascertain any structural changes caused by the cross-linking. Compared with the hydrolysis product of lithiated PIP, the aliphatic cross-linked PIPs are little different when the concentration of *sec*-butyllithium is low. At high [BuLi], the spectra of 1,6-dichlorohexane-PIP has a new small peak at 909 cm^{-1} , which is assigned to the C–H vibration of vinyls [29] that are produced by elimination from 1,6-dichlorohexane. The presence of vinyl groups at high [BuLi] indicates that the coupling reaction between lithiated PIP and 1,6-dichlorohexane must occur, so that the vinyl groups can be incorporated into the polymer. For all other aliphatic-cross-linked PIPs, their FTIR spectra are almost the same as that of the hydrolysis product of lithiated polyisoprene. No remarkable structural changes occur for these aliphatic cross-linked PIPs.

In the infrared spectra of lithiated PIP treated with dichlorobenzene, PIP–DCB, there is a new peak at 700 cm^{-1} , which is the characteristic of monosubstituted benzene aromatic C–H in-plane deformation vibrations. Its intensity increases sharply with an increase in the concentration of *sec*-butyllithium; at [BuLi] 0.065 M, only a very small peak is observed at 700 cm^{-1} . Two additional new strong peaks appear at about 1600 and 1511 cm^{-1} , respectively, which arise from the ring C=C stretching vibrations. The presence of the benzene ring shows the incorporation of aromatic rings into the cross-linked PIP.

Swelling ratio — Fig. 2 shows the swelling ratios of cross-linked polyisoprene obtained from the reaction of lithiated PIP with dichlorinated compounds as a function of the concentration of *sec*-butyllithium. The ratio of *sec*-butyllithium to TMEDA is held constant at 1:1. As the amount of *sec*-butyllithium increases, the swelling ratio decreases for every cross-linked polyisoprene sample in the same series, i.e. as the amount of *sec*-butyllithium increases, the cross-link density increases. At high concentration of *sec*-butyllithium, the swelling ratios decrease more slowly than those at low [BuLi], because of gel formation and elimination reactions. Compared to the PIP–DCB and PIP–DCH, PIP–DCE shows a higher swelling ratio at high [BuLi], while the swelling ratios are similar at relatively low [BuLi]. At high concentration, the coupling reaction is probably more efficient for PIP–DCB and PIP–DCH than for PIP–DCE, because of their longer methylene chain. On the other hand, lithium-chloride exchange may significantly contribute to the cross-linking reaction at the low [BuLi], so the swelling ratio shows a lesser dependence on chain length. The swelling ratios of cross-linked PIP, obtained by the use of dichloro compounds are all lower than those from mono-chloro compounds, i.e. a higher cross-link density is achieved with dichloro compounds.

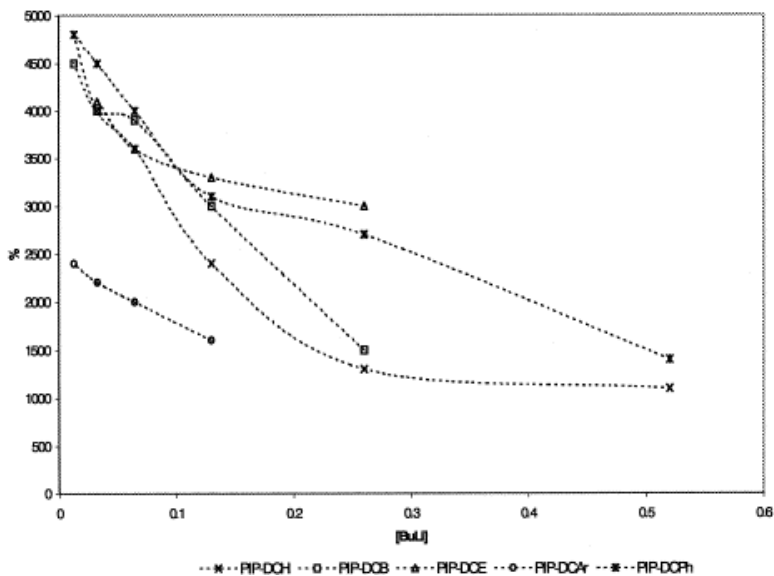


Fig. 2. Swelling ratios of various cross-linked PIP–R–PIP in THF.

The thermogravimetric analysis curves of the lithiated PIP samples that have been cross-linked by the use of dichloro compounds are shown in [Fig. 3](#), [Fig. 4](#), [Fig. 5](#) and the results are collected in [Table 2](#). The TGA curves shown in the figures clearly show the presence of two degradation steps for all of these samples. T_{max} of the first step is very similar to that of PIP–H and is independent of the swelling ratio and the identity of the cross-linking agent. Thus the first step is the degradation of the regions of PIP which are not cross-linked. Because PIP–H shows only a single major degradation step, the second step must involve the degradation of the cross-linked regions. This suggests that the fraction of the polymer which is cross-linked can be obtained, if these two degradation steps are suitably separated. It is clear from the figures that the second step is more important in the material which has been cross-linked with dichlorohexane and α,α' -dichloro-*p*-xylene than for that from dichlorobenzene. The cross-link density is much lower for the sample cross-linked with dichlorobenzene at the same [BuLi] and this is likely the reason the second step is much less pronounced for this material. The higher stability of cross-linking regions may be attributed to the need to rupture more bonds in order to observe mass loss or to the cross-linking groups contributing stronger bonds.

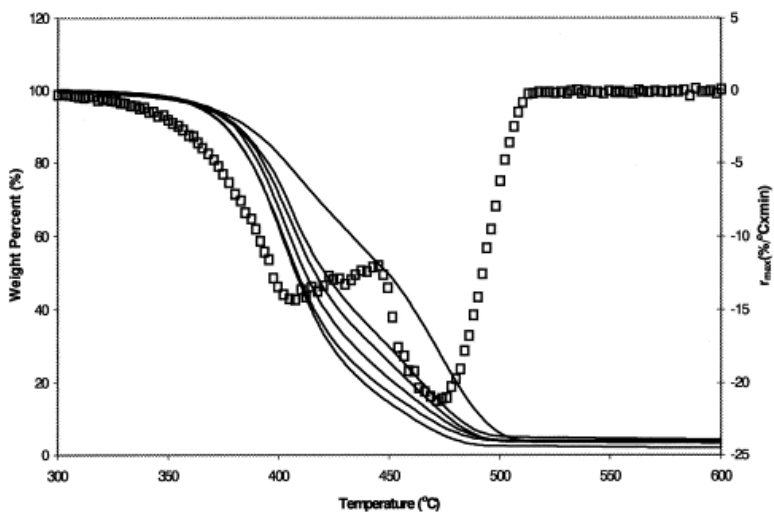


Fig. 3. Thermogravimetric analysis of PIP–DCH at 20°C/mm under N_2 . Solid lines represent various PIP-DCHs crosslinked at different [BuLi]. With increased [BuLi], the TGA curves shift to the right. The dashed lines represents the derivative of PIP-DCH at [BuLi]=0.52 M.

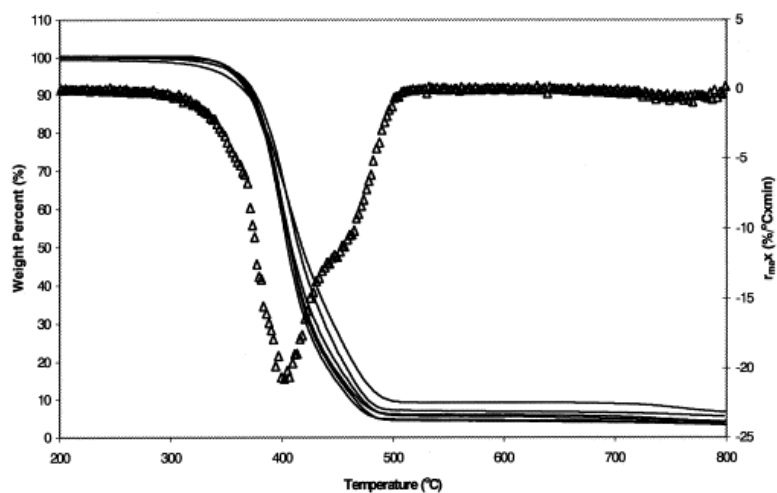


Fig. 4. Thermogravimetric analysis of PIP-DCPh at 20°C/mm under N₂. Solid lines represent various PIP-DCPhs crosslinked at different [BuLi]. With increased [BuLi], the TGA curves shift to right. The dashed line is the derivative of PIP-DCPh at [BuLi] = 0.52 M.

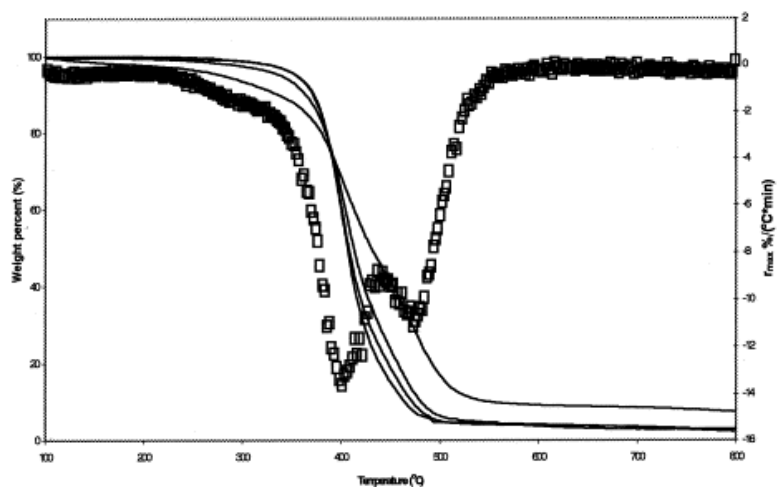


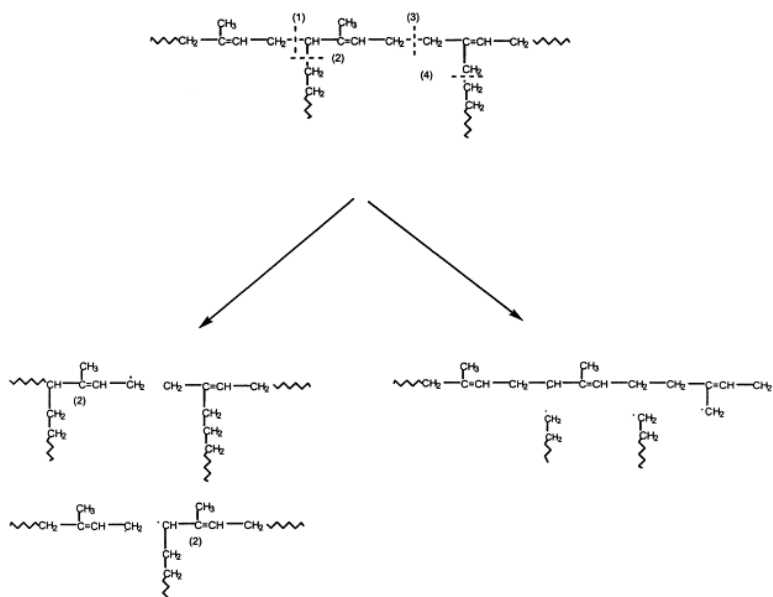
Fig. 5. Thermogravimetric analysis of PIP-DCAr at 20°C/mm under N₂. Solid lines represent various PIP-DCArS crosslinked at different [BuLi]. With increased [BuLi], the TGA curves shift to right. The dashed line is the derivative of PIP-DCAr at [BuLi] = 0.13 M.

Table 2. TGA of cross-linked PIP by dichlorinated compounds

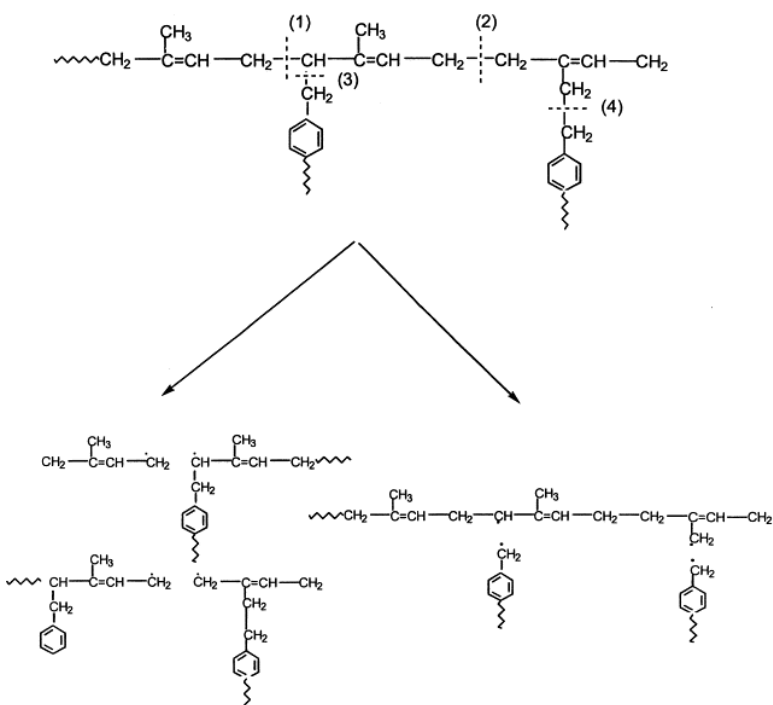
Sample	[BuLi]	SR% (±100)	T3% (±2°C)	T50% (±1°C)	T _{max} (±1°C)	R _{max} (±0.5% min)	Char at 600°C (±1%)
PIP-DCH	0.52	1100	346	443	403	-14.2	3.5
0.26	1300	352	417	404	-25.3	2.0	
0.13	2400	354	412	401	-26.6	2.9	
0.065	3700	355	408	401	-29.9	2.1	
0.033	4000	355	408	401	-30.7	3.5	
0.013	4800	356	407	401	-32.7	2.1	
PIP-DCB	0.26	1500	353	426	407	-23.5	3.1
0.13	3000	351	411	403	-24.8	2.4	
0.065	4000	352	409	403	-29.3	2.6	
0.033	4000	353	408	403	-30.6	3.1	

0.013	4500	353	407	403	-32.8	3.0	
PIP-DCE	0.26	3000	350	412	405	-26.7	2.9
0.13	3300	351	411	405	-28.4	2.6	
0.065	3600	350	410	405	-29.9	2.8	
0.033	4100	356	408	404	-31.7	2.2	
PIP-DCAr	0.13	1600	248	432	404	-13.2	9.3
0.065	2000	316	413	402	-25.3	4.2	
0.033	2200	338	413	403	-29.7	4.0	
0.013	2400	338	409	401	-30.8	3.7	
PIP-DPh	0.52	1400	339	427	406	-18.8	9.7
0.26	2700	346	417	405	-22.4	6.9	
0.13	3100	348	409	404	-25.7	5.0	
0.065	4000	349	406	403	-30.8	3.5	
0.033	4500	352	406	402	-32.9	3.5	
0.013	4800	335	405	402	-31.9	3.0	

T3% decreases as the cross-link density increases for aromatic-cross-linked PIP-R-PIPs while it is rather close to each other for aliphatic-cross-linked PIP-R-PIPs. Compared with the T3% of PIP-H, aliphatic-cross-linked PIP-R-PIPs show similar values of T3% while aromatic-cross-linked PIP-R-PIPs have much lower onset temperature of the degradation at comparable swelling ratios. For example, PIP-DCAr (PIP- α,α' -dichloro-*p*-xylene) and PIP-DPh (PIP-1,4-dichlorobenzene) have T3% of 338 and 346°C at swelling ratios of about 2500, respectively, while PIP-DCH (PIP-1,6-dichlorohexane) and PIP-DCB (PIP-1,4-dichlorobutane) are at 354 and 351°C, respectively. The change of onset temperatures of the degradation for cross-linked PIP-R-PIPs can be rationalized by degradation pathways. For the aliphatic cross-linked PIP-R-PIPs, the initial degradation is believed to occur on the polyisoprene backbone rather than through the rupture of the cross-links. [Scheme 3](#) shows that bond rupture in the main chain is favorable because more stable radicals can be produced from this pathway. In this scheme, cleavage at positions 1 or 3 lead to the formation of two stable allylic radicals while at position 2 or 4, the results are one primary radical and one allylic radical. This degradation pathway is similar to that of virgin PIP which degradation also starts in the backbone, therefore, there is not much difference for their onset temperatures of degradation. For aromatic cross-linked PIP-R-PIPs, the degradation may or may not occur in the backbone, depending on the cross-linked structure. [Scheme 4](#) shows the possible degradation pathways for PIP-DCAr (PIP- α,α' -dichloro-*p*-xylene), cleavage at positions 3 or 4 are favourable as well as that at positions 1 or 2. The change of degradation pathway from that of virgin PIP may account for the earlier onset temperatures of degradation of aromatic-cross-linked PIP-R-PIPs. With the increased crosslinking density, aromatic-cross-linked PIP-R-PIPs show early degradation because the cross-linking process produces more tertiary carbons in the polymer. The more tertiary carbons, the more easily radicals can be produced at an early stage in the degradation and the lower will be T3%.



Scheme 3. Degradation of PIP cross-linked with aliphatic dichloro-compounds.



Scheme 4. Degradation of PIP cross-linked with aromatic dichloro-compounds.

T50% generally decreases with the increased swelling ratio, i.e. with decreased cross-link density, but the tendency becomes clearer for cross-linked PIP with long bridge length, such as PIP-DCH(PIP-1,6-dichlorohexane) and PIP-DCB(PIP-1,4-dichlorobutane), because a larger difference of swelling ratios can be obtained. In contrast to the PIP-PIP, PIP-R-PIP has higher T50% than PIP-H and T50% is no longer equal to the T_{max} . Because the simply cross-linked PIP-PIP has the same TGA curves as PIP-H and their TGA curves are independent of swelling ratios, the groups which are introduced in the cross-linking structures must contribute to the enhanced T50% and to the entire TGA curves. This result shows the importance of the incorporation of cross-linking groups in order to obtain polymeric materials with increased thermal stability, as indicated by T50%.

As the swelling ratio increases, the absolute value of r_{\max} also increases. For example, r_{\max} increases from 14.2 to 32.7% with an increase in the swelling ratios from 1100 to 4800% for PIP–DCH(PIP-1,6-dichlorohexane), and from 13.2 to 30.8% as the swelling ratio increases from 1600 to 2400% for PIP–DCAr(PIP- α,α' -dichloro-*p*-xylene). Because the first degradation step corresponds to the degradation of the region that is not cross-linked, this region results in a high r_{\max} .

Similar to the PIP and PIP–H, the aliphatic cross-linked PIP–R–PIPs and aromatic cross-linked PIP–R–PIPs with high swelling ratios give no char at 600°C, while aromatic cross-linked PIP–R–PIPs with low swelling ratios do have some visible black residue, even at 800°C. For example, lithiated PIP that has been reacted with DCPH gives 7% non-volatile residue at 800°C and the reaction product from DCAR gives 8% char. As discussed above, the initial degradation occurs on the polyisoprene backbone rather than through the rupture of the cross-links for the aliphatic cross-linked PIP–R–PIPs because more stable radicals can be produced. Polyenes, which are char precursors, are thus not formed, and hence significant char is not formed. [Scheme 4](#) shows that regardless of where the initial degradation occurs, the aromatic ring is incorporated into the new backbone for PIP–DCAR (PIP- α,α' -dichloro-*p*-xylene), which is similar to the linear aromatic containing polymers, and would be expected to produce char from the aromatic content. An alternative pathway for degradation involves the potential formation of polyenes, and these will also enhance char formation. The degradation of an aromatic cross-linked PIP is expected to enhance char formation. The low char yields observed for aromatic cross-linked PIP–R–PIPs with high swelling ratios is attributed to their low degree of aromatic ring incorporation.

4. Conclusion

The lithiation of squalene and of polyisoprene takes place by the exchange of lithium and an allylic hydrogen atom. Lithiated PIP may be reacted with both monochloro compounds and dichloro compounds and cross-linked products are obtained in both cases. The cross-link density is quite low for materials formed from monochloro compounds and there is no change in the thermal stability compared to virgin PIP or the hydrolysis product of lithiated PIP. The onset of the thermal degradation occurs earlier for all cross-linked PIPs but one can see a difference in the temperature required to achieve 50% degradation. PIPs which have been cross-linked with aromatic dihalides show significant non-volatile residue at elevated temperatures while the aliphatic materials do not produce significant char. It is apparent that the nature of the cross-link is the most important factor to determine thermal stability of these cross-linked polymers.

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