Modification and cross-linking of saturated elastomers using functionalized azides

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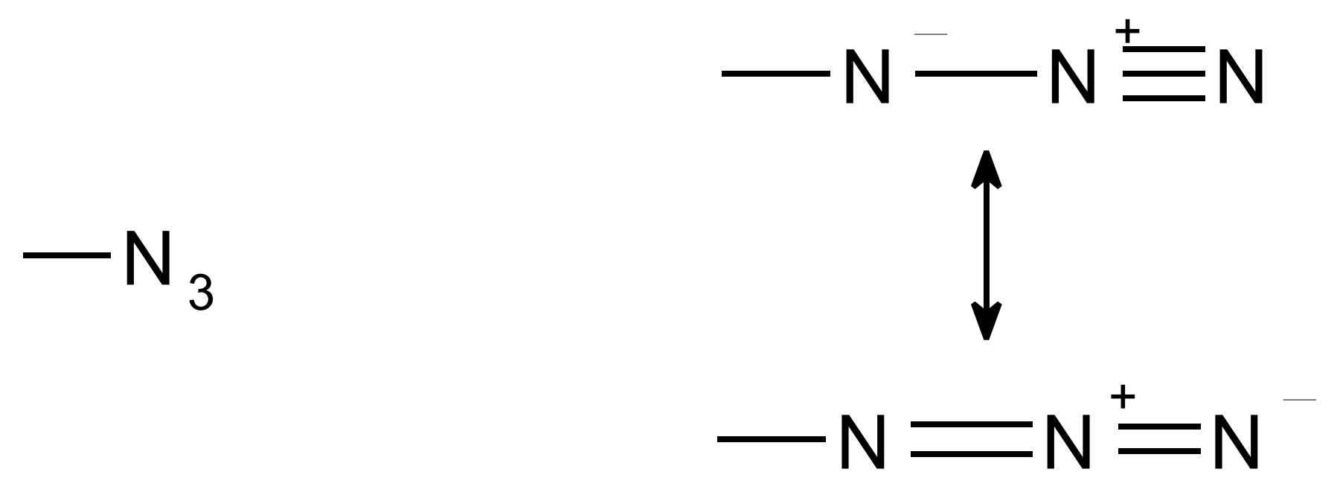
Introduction

1. The azide group



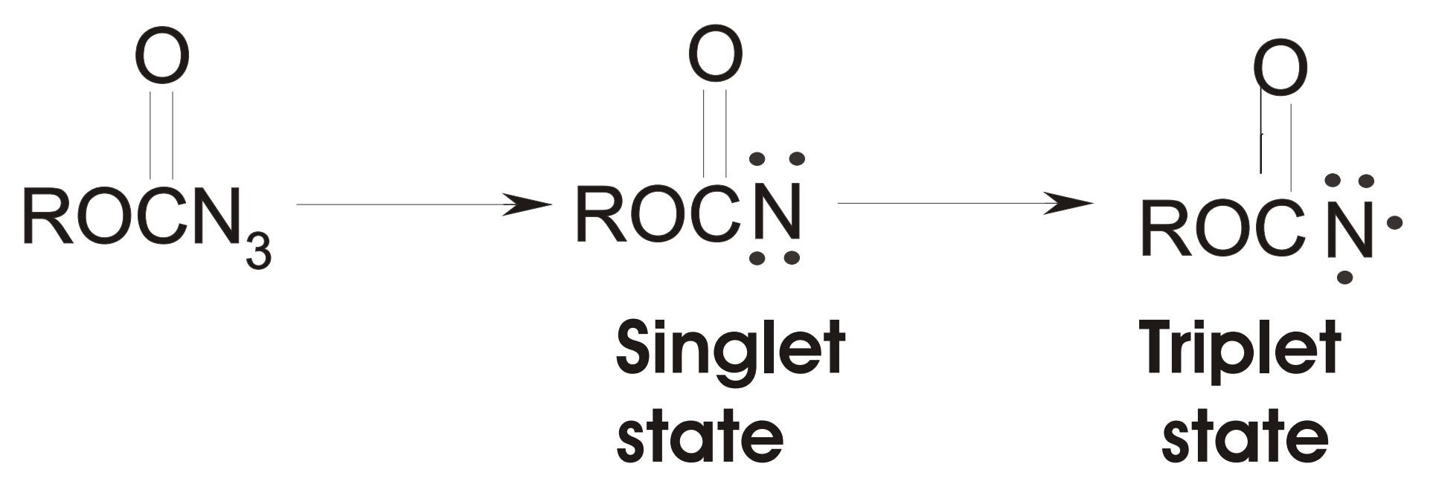
- Known to exist for over 100 years.
- Little or no interest until 1950's.
- Used as a source of nitrenes.

The azide group can decompose photo-chemically or thermally, releasing a nitrogen molecule and yielding a highly reactive nitrene species.

$$R{-}N_3 \xrightarrow{h\nu/\ T} R{-}\ddot{N}{:} + N_2$$

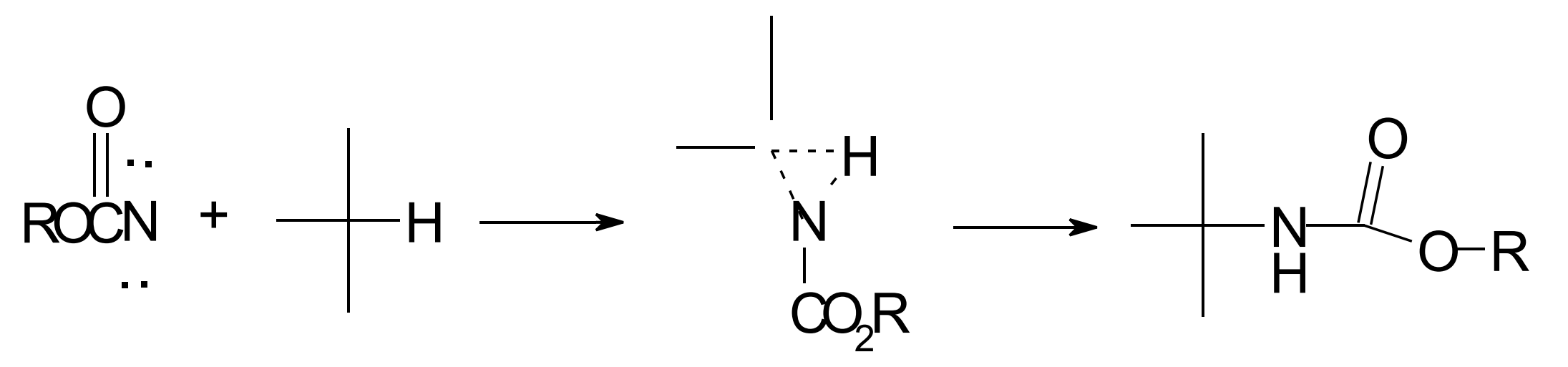
2. Decomposition of azides

Initially a nitrene is formed as a singlet, with paired electrons (the preferred state). It may, however, progress to the more stable triplet state.

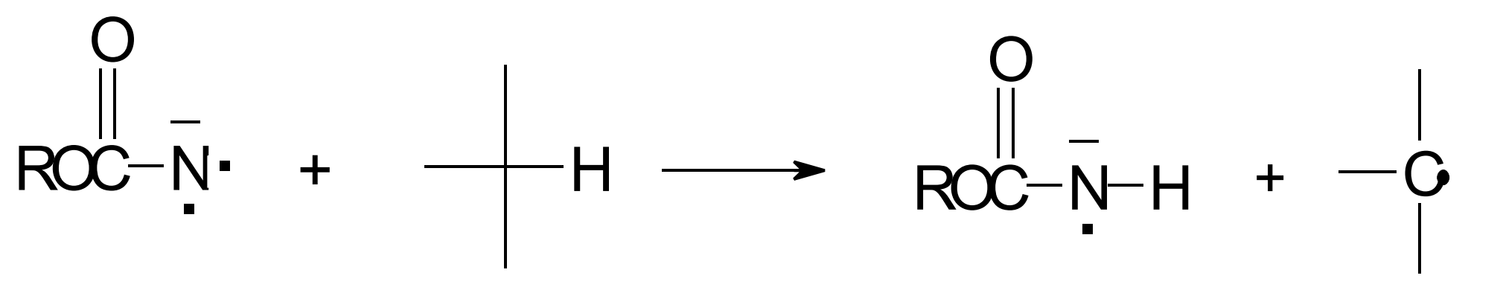


3. Reactions

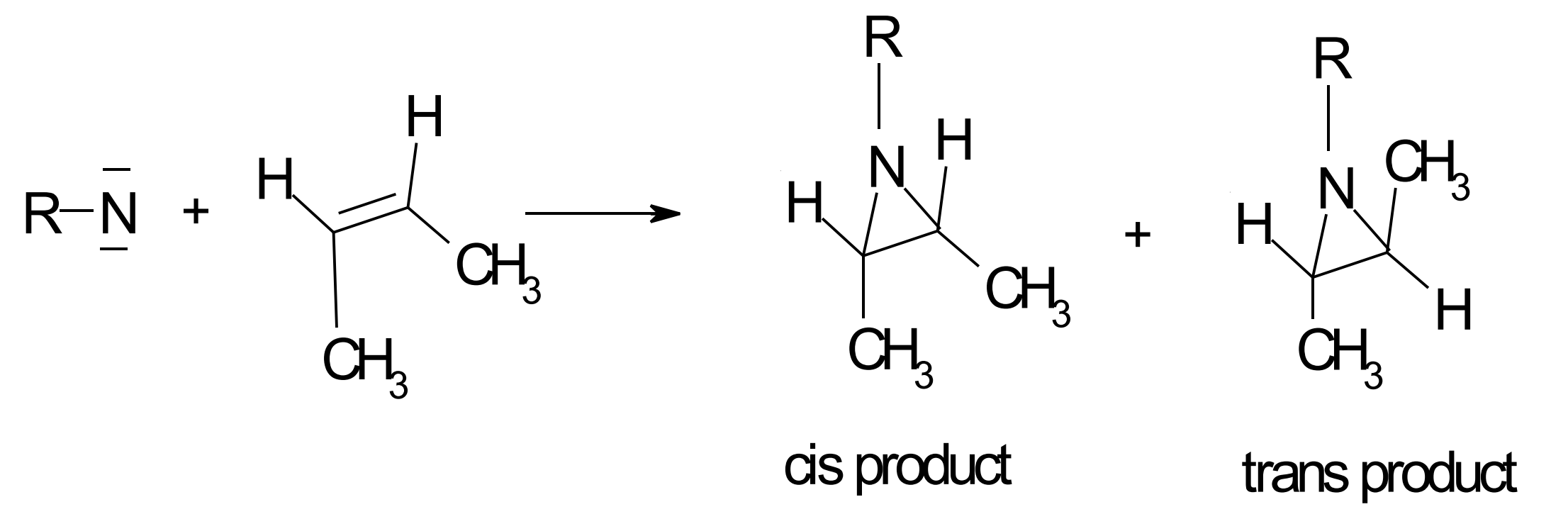
Only the singlet state of nitrene readily inserts into saturated carbon-hydrogen bonds.



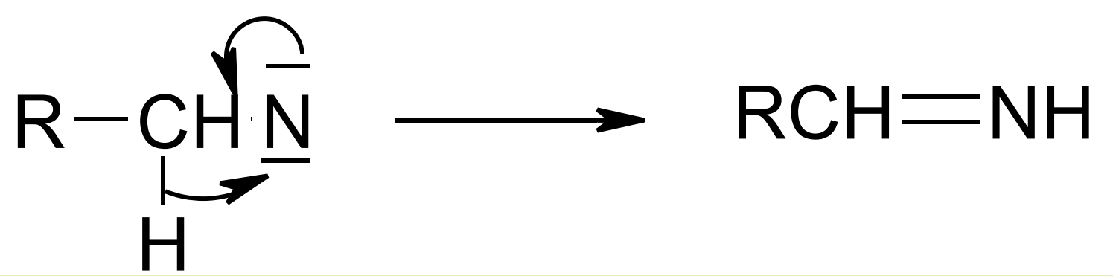
The triplet state of nitrene can abstract hydrogen atoms to give free radicals.



Both, singlet and triplet state of nitrenes can react with double bonds.



Alkyl nitrenes can undergo rearrangement, with 1,2-H shift.

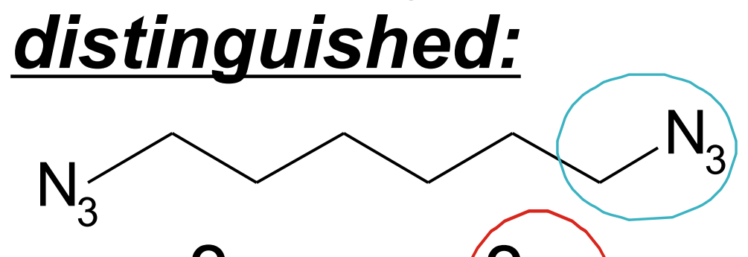


Cross-linking

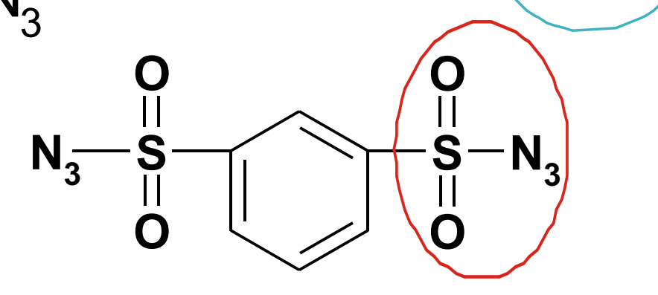
The problem with cross-linking of saturated elastomers is their low reactivity: saturated chains react only under very specific conditions and by a very limited number of reactions. The common way to overcome the lack of reactivity is by pursuing free-radical reactions with peroxide. Azide reactions could be an alternative with much higher cross-linking efficiency and reduction of polymer degradation.

Cross-linking of polymer chains by a substance containing at least two azide groups can be achieved as a result of the reaction of two azide groups with different polymer chains.

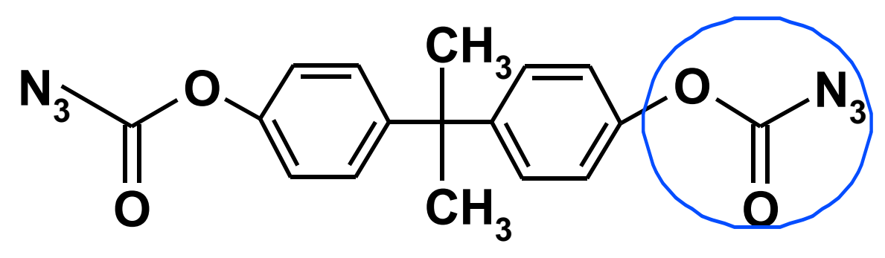
Different types of azide functionality can be distinguished:



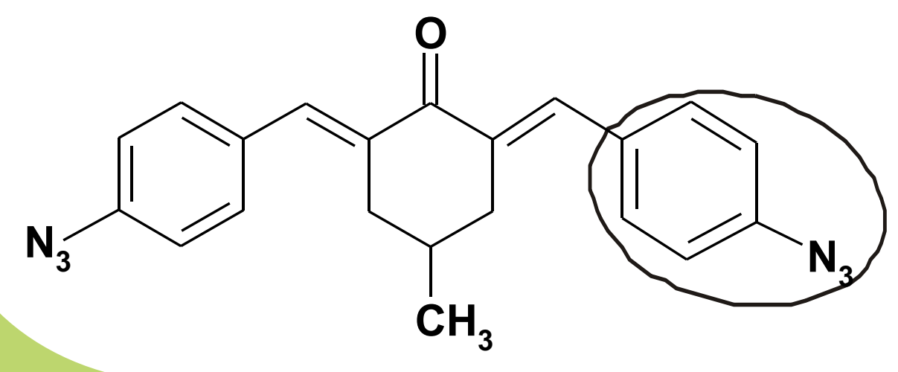
Aliphatic azide (ADA)



Sulfonyl azide (DSA)

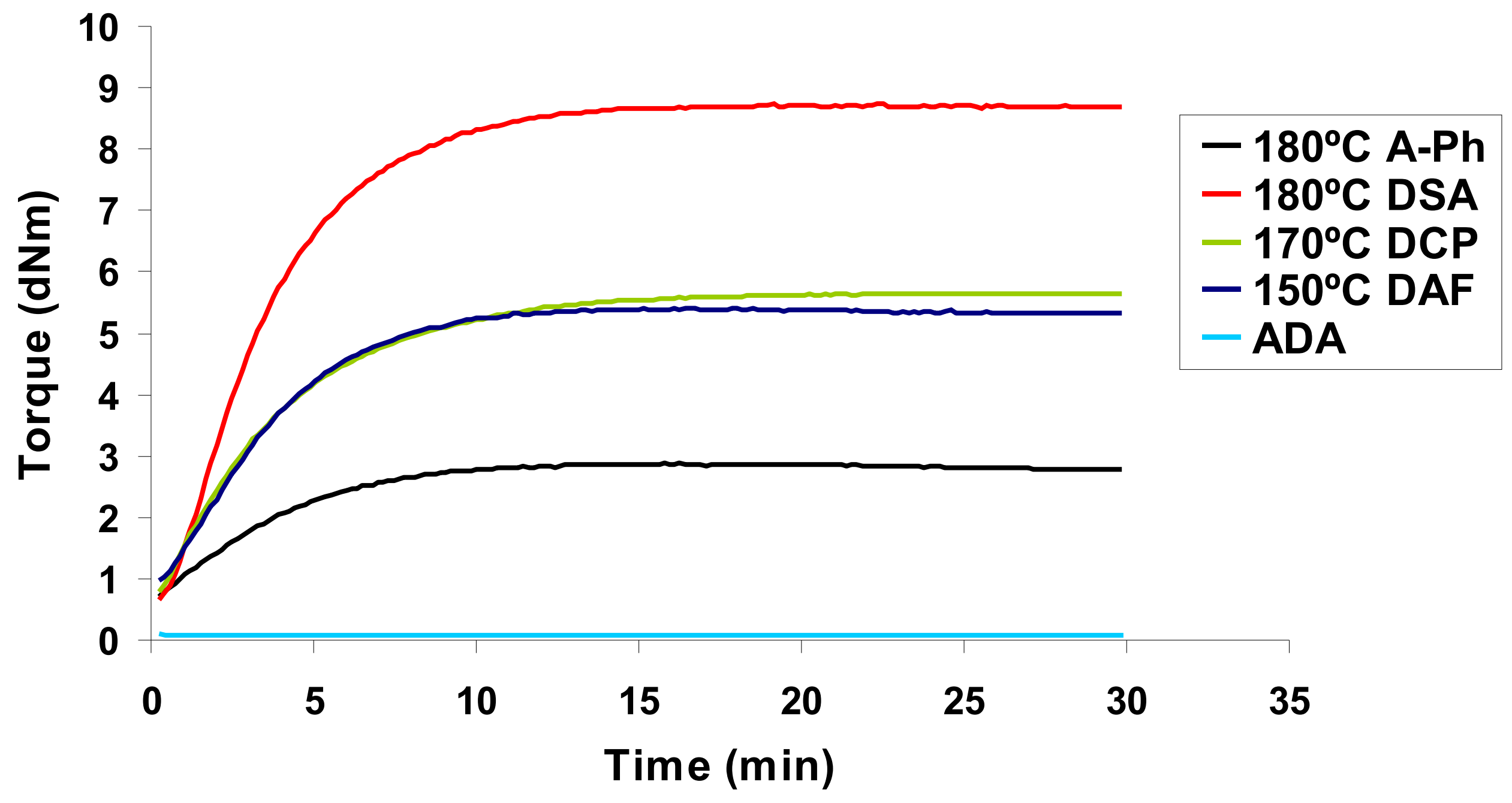


Azidoformate (DAF)



Azido phenyl (A-Ph)

Cross-linking of EPM



Rheogram of samples containing different azides and dicumyl peroxide (DCP)

Different azide types are reacting in a different manner and also at various temperatures. Only two of them can be applied as curing agent for saturated elastomer.

Polymer modification

The azide can be synthesized so as to contain a functional group which will affect the properties of the treated polymer. The modification process can be carried out by reactive mixing at a temperature above the azide decomposition temperature.

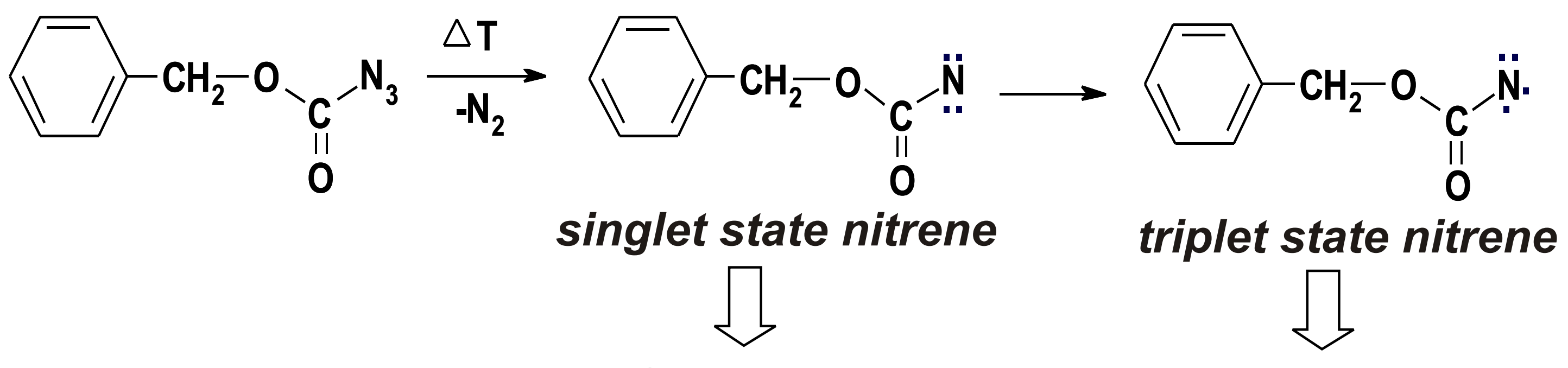
Solubility of modified EPM

Azide amount (phr)	temp. (ºC)	Hexane		THF	
		<5h	<24h	<5h	<24h
0.75	150	+		+	
	160	+		+	
	170	+		+	
1.5	150		+		+
	160		+		+
	170		+		+

Azide amount (phr)	Reaction time	temp. (ºC)	Hexane (days)		THF (days)	
2.25	10min	150	7	6	17	10
	10min	160	6	3	8	3
	3min	170	3	3	1	2

Example:

EPM was modified with different amounts of benzyl azidoformate (BAF).

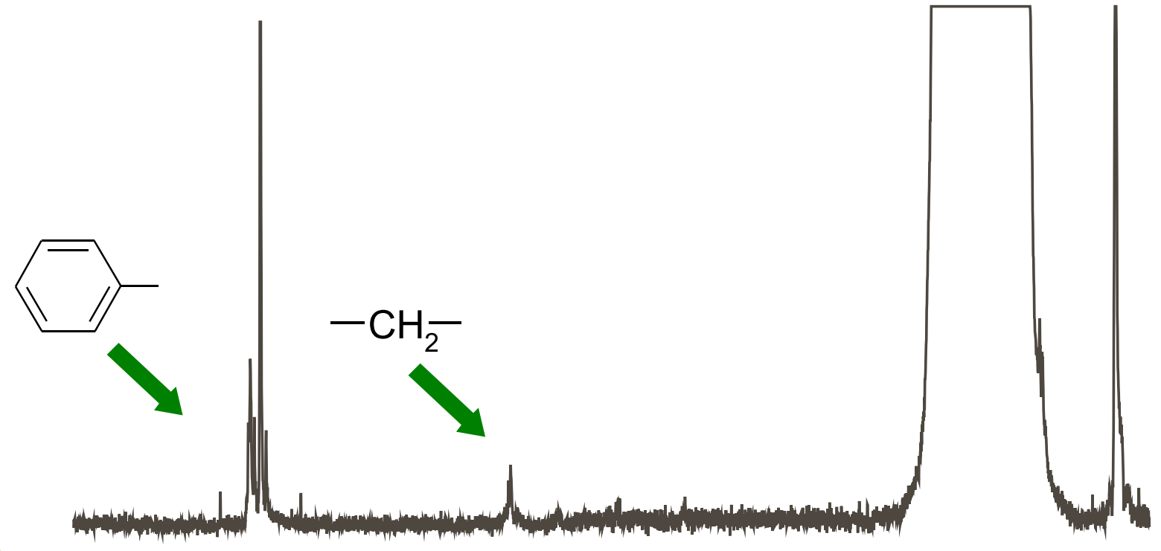


Grafting efficiency

Azide amount (phr)	Start temp. (ºC)	Before purification (%)	After purification (%)
0.75	150	52	52
	160	52	52
	170	68	51
1.5	150	43	43
	160	43	43
	170	60	34
2.25	150	52	46
	160	53	46
	170	58	47

H1 NMR spectra

Pure EPM



EPM after modification

Conclusions

- Curing of EPM using di-azidoformate, disulfonyl azides and di-azidophenyl does occur.
- Modification of EPM with substances containing azidoformate group is possible. By using azido compounds with a second functional group a reactive moiety can be attached to the polymer.
- The azidoformate group has the lowest decomposition temperature.

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