(3*E*,11*E*)-trideca-1,3,11-trien-5,7,9-triyne

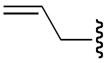
The above compound is part of a plant defense mechanism (anti-nematode) from canola to kill predatory worms.

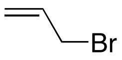
All double bonds and triple bonds in the above compound are conjugated.

It is a derivative of a tridecane (13 carbons). Know the names of the first 20 alkanes. Begin numbering at the end of the longest chain with maximum number of multiple bonds so as to give the first multiply bonded carbon the lowest number. There is no stereochemistry in the triple bonds because they are linear (180°). Stereochemistry is only potentially possible in the double bonds.

**Nomenclature of Allyl and Vinyl Groups** (the squiggly line represents attachment to any group)

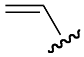
Allyl Group Example

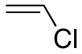




allyl bromide

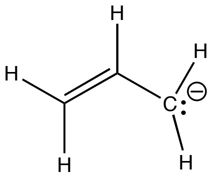
Vinyl Group Example





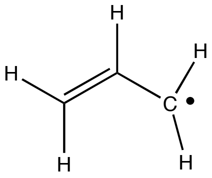
vinyl chloride

Allyl (Allylic) intermediates include:



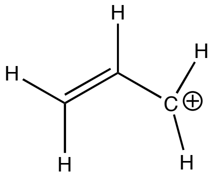
Allyl anion

Has 8 $e^-$ at C
C is negative



Allyl radical

Has 7 $e^-$ at C
C is neutral but reactive



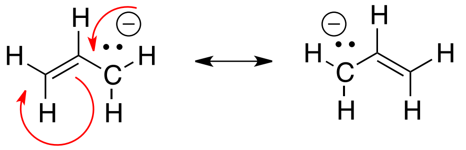
Allyl cation

Has 6 $e^-$ at C
C is positive

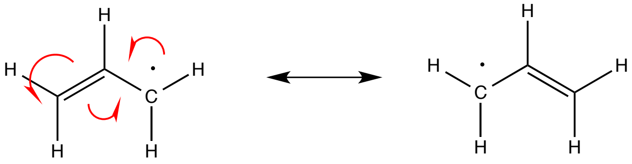
All are conjugated intermediates. The excess or deficient electrons at the carbon atom are conjugated to the double bond.

All are stabilized through resonance structures.

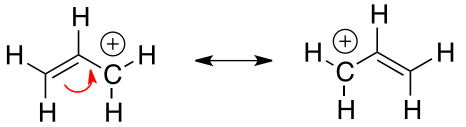
Allyl Anion:



Allyl Radical:

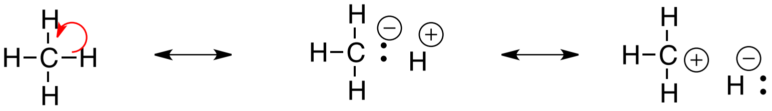


Allyl Cation:



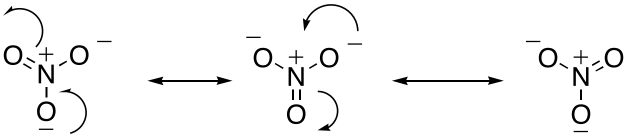
## Resonance Forms

Resonance forms (resonance structures) are different pictures of the same molecule obtained by moving electrons without changing the position of the atoms.



separation of charge is BAD

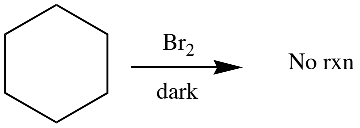
Shown below are the resonance forms of sodium nitrate ($NaNO_3$). The anion on oxygen is a conjugated anion. Resonance forms are connected by a double headed arrow.

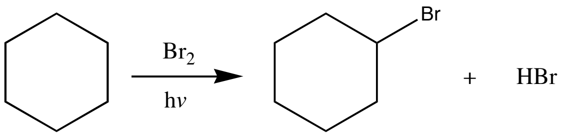


## Review of Reactions

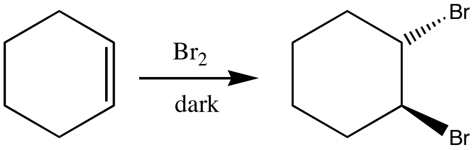
(note: reaction will frequently be abbreviated as “rxn” in this course)

### Substitution:

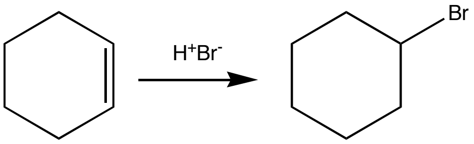




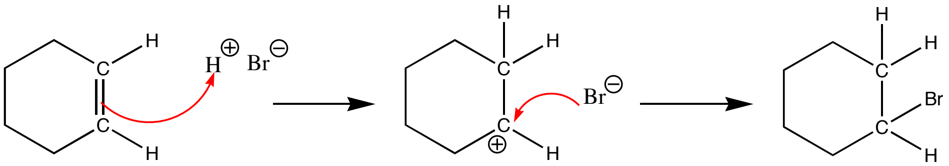
### Addition:



fast

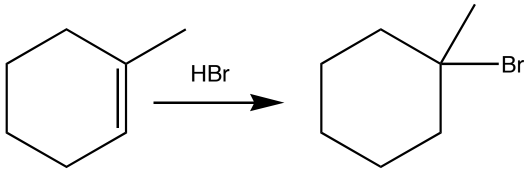


### Mechanism:

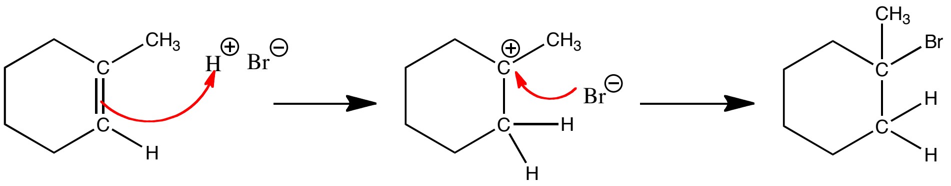


Carbocation intermediate

An example of a reaction following the Markovnikov Rule:



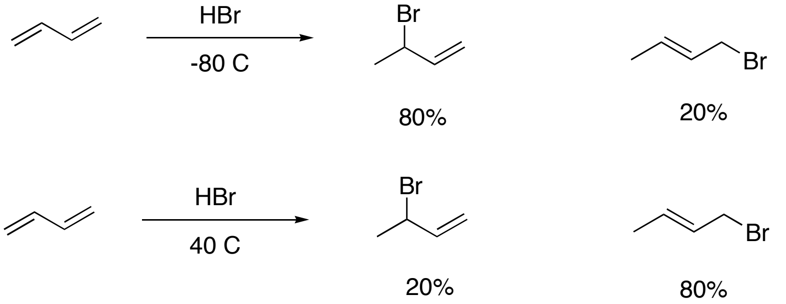
1-methylcyclohexene



the $3^{o}$ carbocation is the most stable,
it has more groups stabilizing
the postive charge

Stability of carbocations: allylic > $3^{o}$ > $2^{o}$ > $1^{o}$> $^{+}CH_3$

**Addition Rxn of Conjugated System**



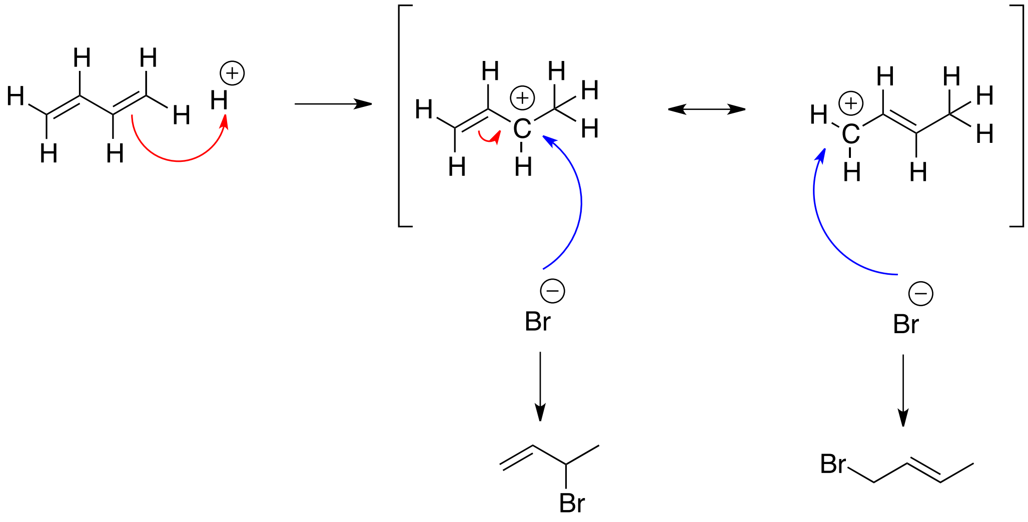
1,3-butadiene 3-bromo-1-butene 1-bromo-2-butene

These are structural isomers.

The product 3-bromobutene is a **1,2-addition** product, whereas 1-bromo-2-butene is the product of an **1,4-addition** reaction. The numbers (**1,2-** or **1,4-**) indicate the position where the H and Br added to the 1,3-butadiene. 3-Bromobutene had hydrogen and bromine atom added to C**1** and C**2** of 1,3-butadiene (hence **1,2**-addition), whereas in 1-bromo-2-butene, the hydrogen and bromine atoms are added to C**1** and C**4** of 1,3-butadiene (therefore it is an **1,4**-addition).

Why does the temperature affect the ratio obtained?

To understand, look at mechanism of the reaction:



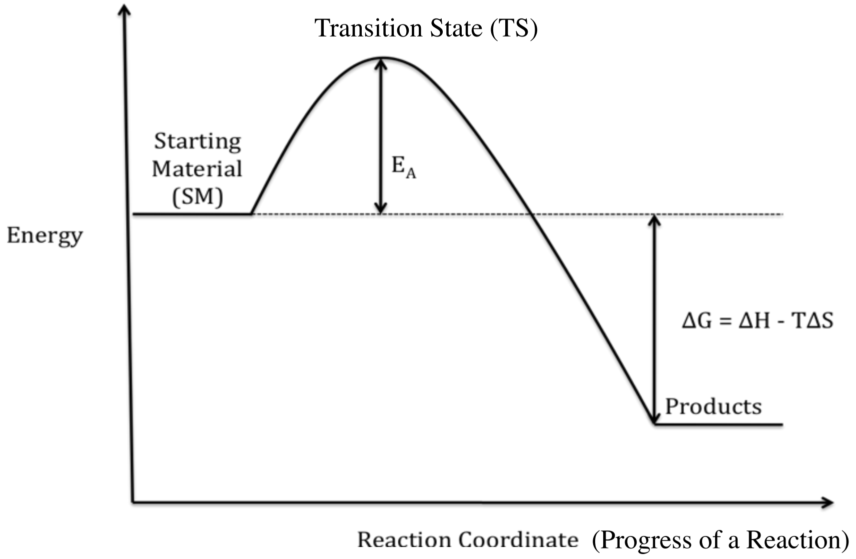
From the 2 resonance forms (connected by the double-headed arrow) of the allylic cation shown in the above figure, we see that the positive charge is shared between the two carbons (C2 and C4) with each carrying a portion of the positive charge.

*Note*: the allylic cation has two electrons delocalized across the three carbons. It was drawn to have two resonance forms, but it is a ***single entity***, therefore we cannot differentiate and speak of one form being a primary carbocation (therefore less stable) and the other being a secondary carbocation (therefore more stable).

***Answer to the above question*:**

- 3-bromo-1-butene has a higher yield at the lower temperature because it is kinetically more favoured. It formed faster than 1-bromo-2-butene. **Kinetic Control**
- 3-bromo-1-butene has lower yield than 1-bromo-2-butene at higher temperature due to **thermodynamic control**. The addition of bromine to the allylic cation is reversible at high temperature. 3-Bromo-1-butene can be converted back to the allylic cation and then form 1-bromo-2-butene, which is the thermodynamically more favoured product.

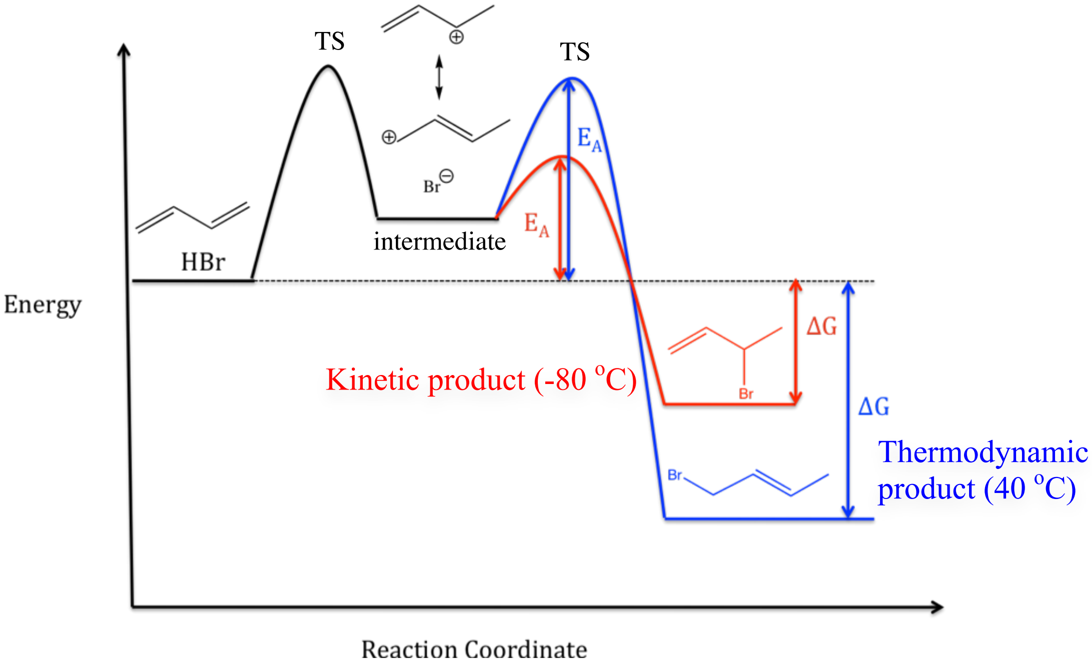
To understand thermodynamic and kinetic control let's begin by looking at the energy diagram of a reaction.



$\Delta G$ = free energy of the reaction – this determines ratio of starting material and product
$\Delta H$ = enthalpy of the reaction
T = temperature in (degrees) Kelvin
$\Delta S$ = entropy
$E_A$ = activation energy (the amount of energy needed for reaction to proceed). This is a factor that determines the rate of a reaction. When $E_A$ is small, the reaction is fast and when it is large the reaction is slow.
Transition State (TS) = bonds are partially made and partially broken

For an exothermic reaction, there is release of heat and $\Delta G$ is always negative (depicted in the energy diagram, the starting material would be higher on the energy diagram than the product).

Now let's look at the energy diagram of our butadiene and HBr addition reaction

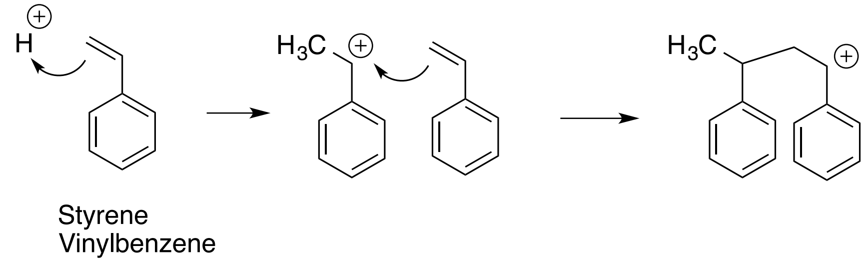


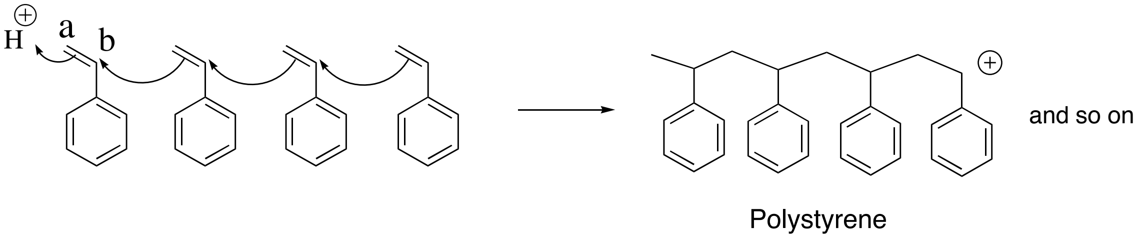
One thing to point out in the energy diagram is that the activation energy barrier to form the 1,2-product 3-bromo-1-butene is much *smaller* than the 1,4-product 1-bromo-2-butene (so that it can be formed easier and **faster**. We call this **kinetically** favoured). However, the energy of 1-bromo-2-butene is lower than 3-bromobutene, so that it is more **stable** than 3-bromo-1-butene (we call it the **thermodynamically** favoured product). (Why is 1-bromo-2-butene more stable? This could be explained as follows: the bromine atom is bulky. It likes to stay away from the rest of the molecule to avoid steric clashes. In addition as alkene carbons are somewhat electron deficient, more highly substituted alkenes are often more stable due to donation of negative charge by the substituents)

At low temperature, the lower activation energy pathway (coloured red in diagram) dominates and the reaction proceeds to form 3-bromo-1-butene. There is not enough energy for most molecules to overcome the $E_A$ barrier to form large amounts of 1-bromo-2-butene. At high temperature, there is a large amount of energy available to overcome the $E_A$ barrier forming 1-bromo-2-butene (coloured in blue). Since the bromine addition to the allylic cation is reversible, 3-bromo-1-butene can be reversed back to the allylic cation which can then form 1-bromo-2-butene. This is why the yield of 1-bromo-3-butene is high at a high temperature.

## Practical Applications for Conjugated Addition Reaction:

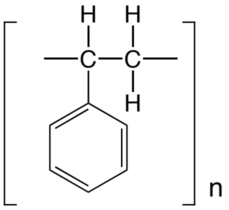
<u>Example: Polystyrene formation</u>





The resulting carbocation is conjugated with the benzene ring and is also 2°.

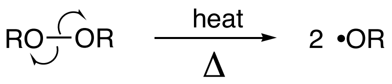
Drawing convention for polymers

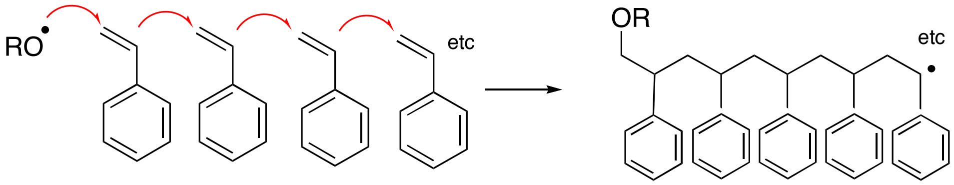


Polystyrene

<u>Example: Polystyrene formation via a radical mechanism</u>

When peroxides are heated, peroxy radicals can be formed:

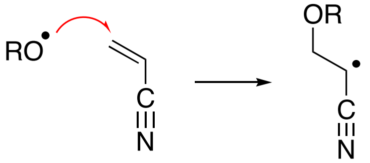




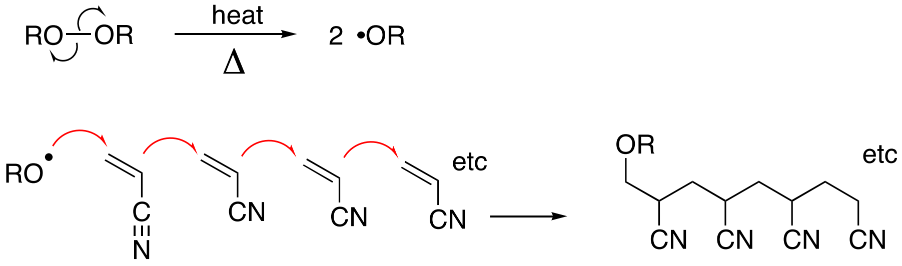
The peroxy radical can add on to the double bond, forming a carbon-based radical. The radical formed is more stable in the benzylic position adjacent to the phenyl ring. This radical can then add onto another molecule of styrene, thus forming a polymer.

Example: Polyacrylonitrile (Orlon) synthesis (by a conjugated radical process)

This example is similar to the radical mechanism of polystyrene formation.

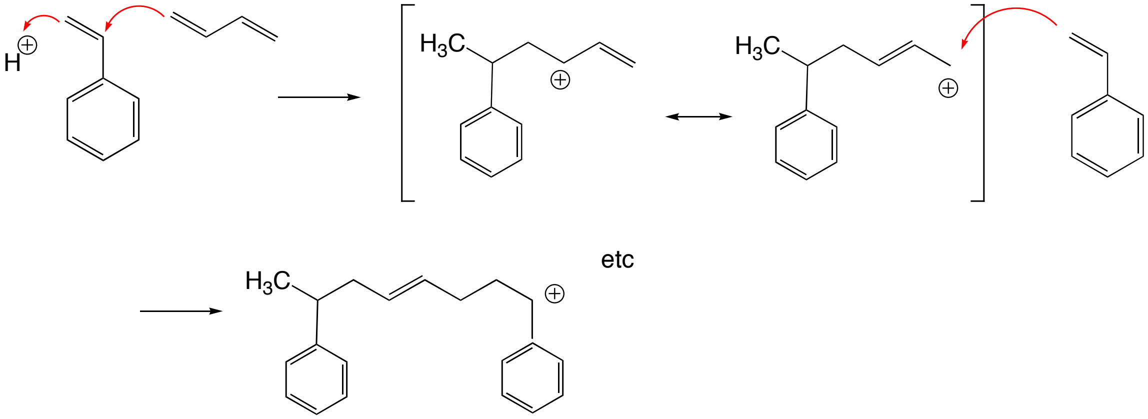


The radical formed on the carbon is stabilized by the adjacent cyano group.

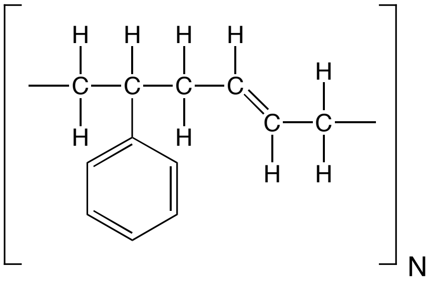


Example: Styrene Butadiene Rubber (SBR) synthesis

SBR is a **copolymer**.

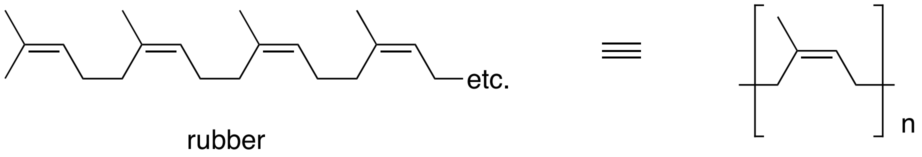


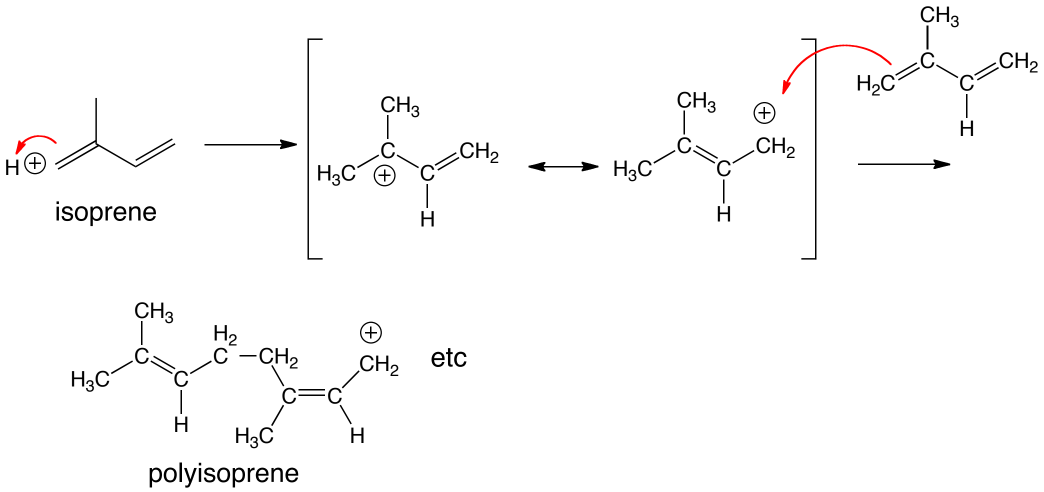
Another representation:



### Example: Rubber formation

Rubber is a natural product produced by rubber tree *Hivea brasiliensis*. The rubber is collected in the form of syrup (latex) and after concentration as raw rubber it is very sticky (like chewing gum). This is not very useful.





Rubber can be viewed as a polymer of 2-methyl-1,3-butadiene, which is also known as isoprene. Addition of acid will form a resonance-stabilized cation.