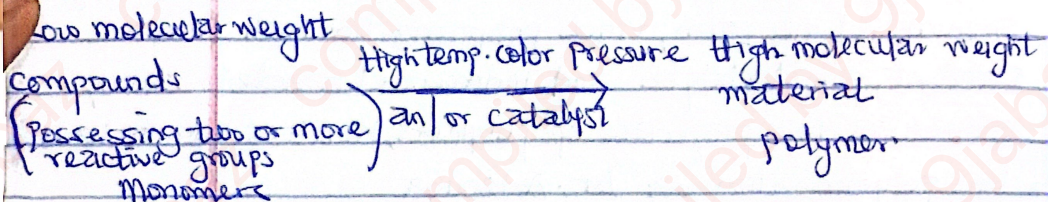


POLYMERIZATION

It is a process by which low molecular weight compounds are converted to high molecular weight compounds which can possess one or more reactive groups. This undergoes high temperature or pressure and catalyst.

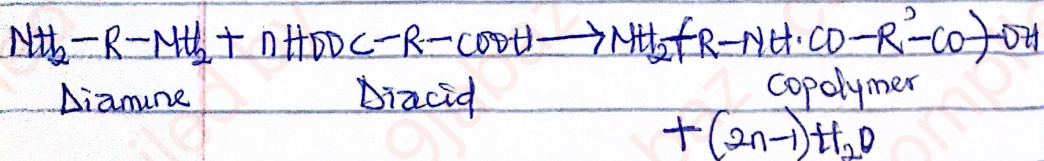


The monomer must have two or more reactive groups e.g. In polyamide

polyamide \Rightarrow An amino group or carboxyl group are involved.

Different types of monomers combine to form a polymer chain called copolymer.

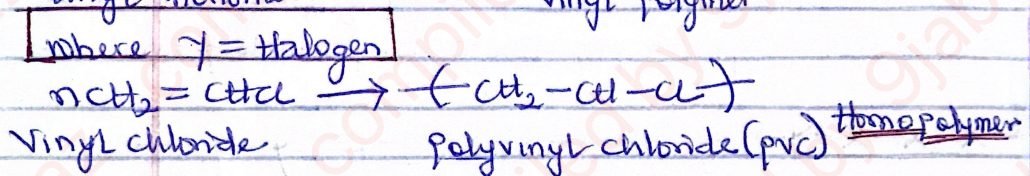
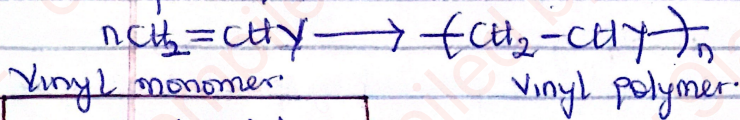
Amino group ($-\text{NH}_2$) carboxyl group ($-\text{COOH}$)



The copolymer formed is a polyamide

This is an example of condensation polymerization which always

result in the formation of a copolymer and a small molecule (H_2O) . In the alternative reactive ^{group} may be double bond e.g. the vinyl polymerization. This is generally represented as follows;



In this case note that a single type of monomer combine to form a polymer called homopolymer.

Quest? Differentiate b/w copolymer & homopolymer with a balanced equation

polymerization process is divided into three (3) categories

- (i) Addition polymerization
- (ii) Condensation polymerization
- (iii) Ring opening polymerization

COPOLYMERIZATION

Copolymerization is the mixture of two or three different monomers ^{to} ~~inter.~~ ^{or give} ~~to~~ ^{to} give copolymers.

CATEGORIES OF COPOLYMERS

(i) Copolymers can be random when we have random arrangement of the two monomers α and γ along the polymer chain e.g.



(i) Random polymer.

DR

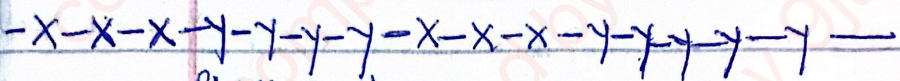
Alternating copolymer as shown below



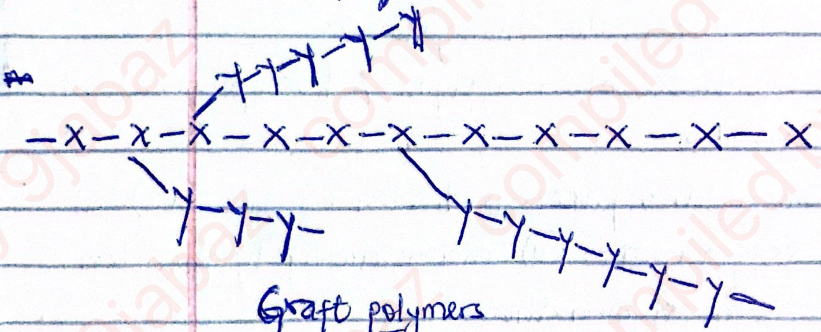
(2) Alternating copolymer

(3) Block and graft copolymers.

This are special copolymers produced by special techniques to give certain specific properties to the products formed.



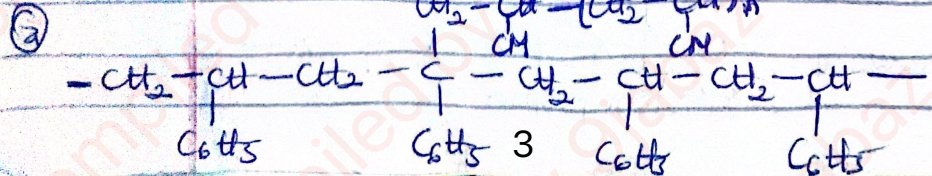
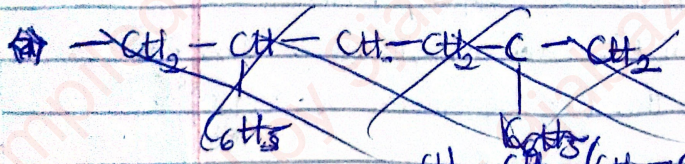
Block Copolymer.

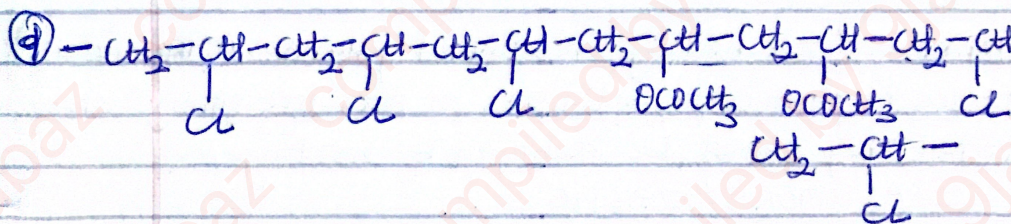
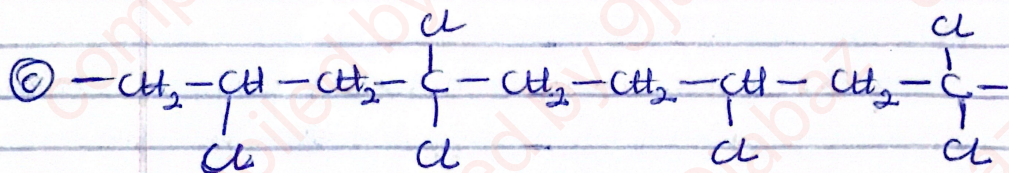
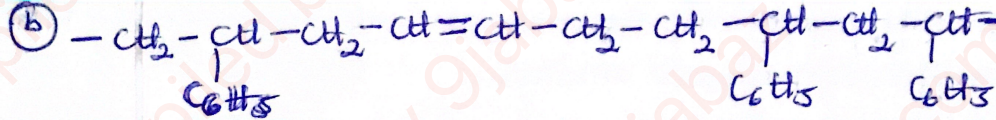


Graft polymers

Questions: 1

(i) classify the following as random, alternating, block or graft polymers





POLYMER BLENDS

In order to modify the properties of polymer two or more polymers are blended. The processing brings about increasing importance of polymer blends in the industry. The blending of polystyrene, for example which is brittle with natural rubber or butadiene-acrylonitrile copolymer for example gives superior product of enhanced impact strength. For the commercial preparation of polymer blends, the polymers are either ground together or melt processed. In this way polymer blends of poly(vinyl chloride) - poly(methyl acrylate) in (50:50 ratio) and poly(vinyl chloride) - poly(vinyl acetate) in (50:50 ratio) are obtained. The ratio can be varied according to the properties desired in the polymer blend.

Generally, properties of Copolymers include their ability to be thermoplastics, thermoset or elastic

WHAT ARE THERMOPLASTICS?

Thermoplastics are linear or branched polymers. They can be repeatedly softened by heating and ~~then~~ solidifies by cooling

THERMOSETS

Thermosets are heavily crosslinked polymers. A thermosetting plastic or thermoset ^{or resin} solidifies or sets irreversibly when heated they cannot be reshaped by heating

ELASTOMERS / ELASTIC

They are rubbery polymers that can be stretched easily to several ~~th~~ times their unstretched length and which rapidly return to their original dimension when the applied strength is released. Furthermore, the properties of Copolymers is that it can be foreseen that in terms of the following based on the usage to which they are used

(i) Density

This is because Copolymers have varied molecular weight resulting from chain complexity.

(ii) Tunability

Copolymers can be designed with a high degree of ^{precision} ~~position~~ in selecting and adjusting properties by choice of monomers, their proportions and ^{the} mechanics of chain construction

(iii) Melt flow: Many copolymers are easily processed using standard thermoplastic techniques like injection molding

(iv) Flexibility/Elasticity/Rigidity:

Copolymers can be tuned to be flexible or rigid depending on the choice of monomers & molecular complexity/simplicity of the construction.

(v) Chemical Resilience: copolymers are often designed for specific resistance to group of chemicals

(vi) Thermal stability: Copolymers usually have widely varying and adjustable degrees of thermal stability

(vii) Electrical conductivity: certain copolymers have been manufactured to conduct electricity

(viii) Optical clarity: Some copolymers are transparent and optically clear

(ix) Biocompatibility: Some copolymers can be engineered to be biocompatible for use in medical implants and treatment systems

(x) Adhesion: Some copolymers have been developed ^{for} strong adhesion to various classes of materials.

(xi) Flame resistance: Copolymers can also be designed for flame retardancy

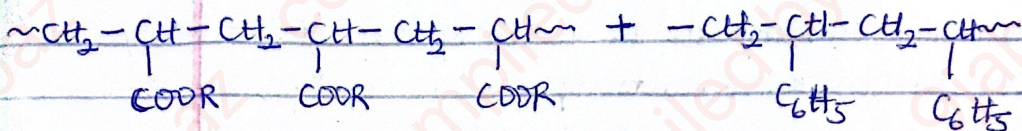
3rd May 2024

BLOCK AND GRAFT CO-POLYMERS

A Synthesis of Graft CO-polymers

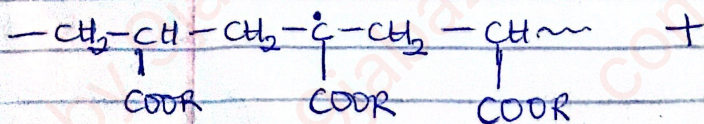
sequence describe

1) By chain transfer! The following reaction expresses the chain transfer which occur when styrene is polymerized in the presence of dissolved poly(acrylate). Example;

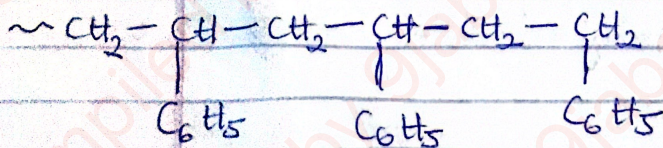


Original polymer
poly(acrylate)

Growing poly(styrene)
chain

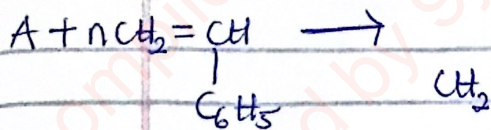


A



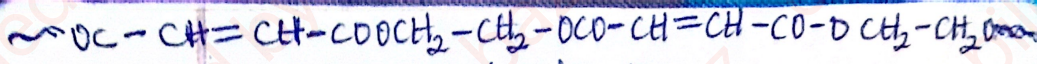
Radical is capable of reacting with a mole of styrene

By Redox Initiation

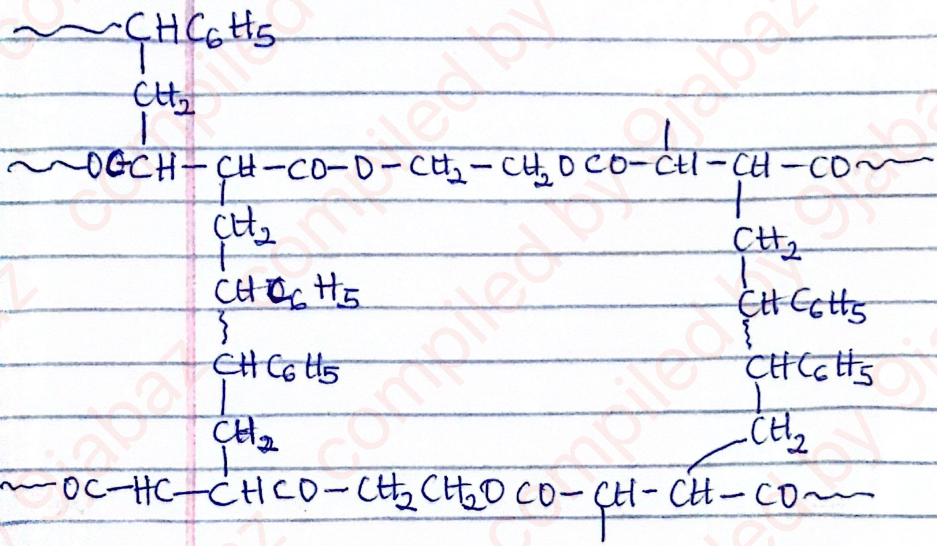
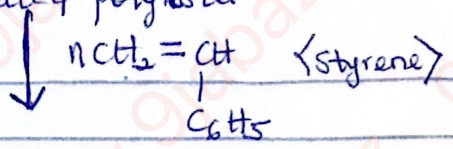


10th May 2024

5) Through Copolymerization: This is achieved when one dissolves an unsaturated polymer in the monomer to be grafted on and allow the monomer to polymerize. The double bond of the polymer is then incorporated into the growing chain of the polymerizing monomer. For example the graft polymerization of unsaturated polyesters



Unsaturated polyester

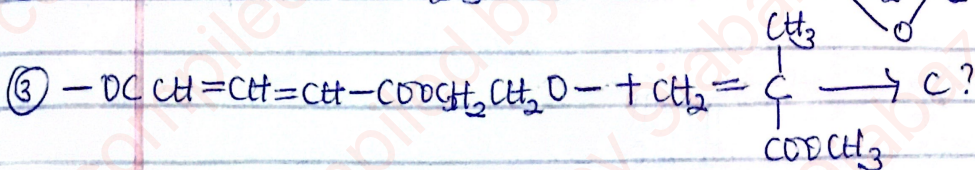
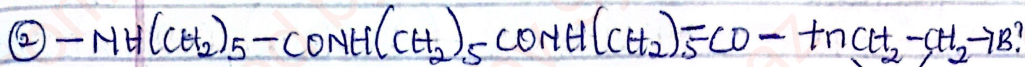
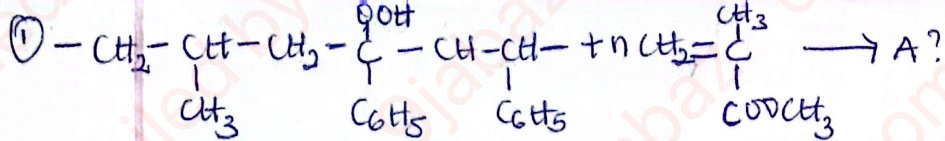


⑥ Grafting by Irradiation:

Irradiation such as X-rays, gamma-rays are capable of producing radicals in organic molecule. If one irradiates the solution of the polymer in the monomer one obtains the same type of reaction that occurs in the chain transfer i.e. the ~~primary~~ ^{polymer} chain of the primary polymer radical is formed. This then becomes the point of initiation for the side chain.

Practice Questions

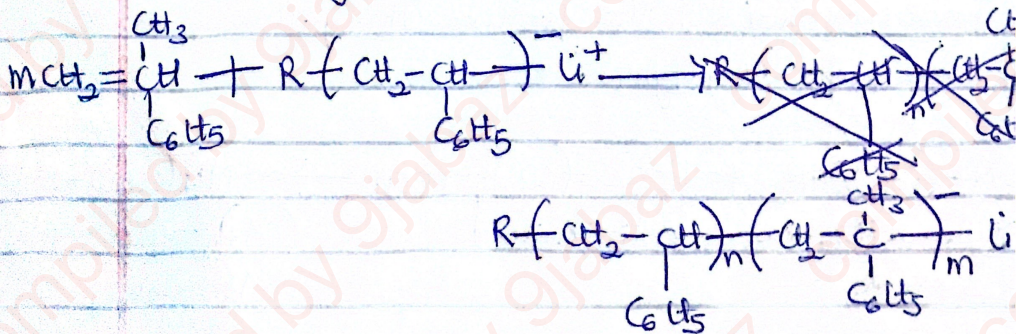
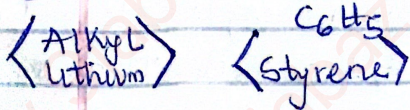
Copy and complete the following reactions in the synthesis of graft copolymers.



Synthesis of block polymer

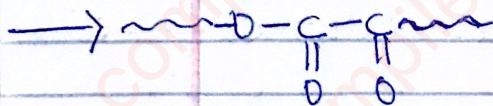
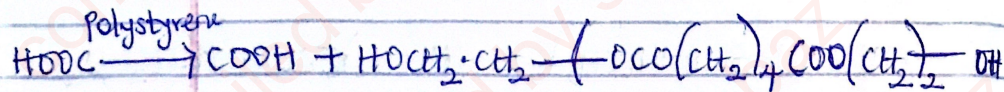
In this case two possible roots exists for the synthesis of block co-polymers which are similar to those used in the formation of graft copolymer. They are as follows-

① polymerization of a second monomer onto an existing polymer chain.



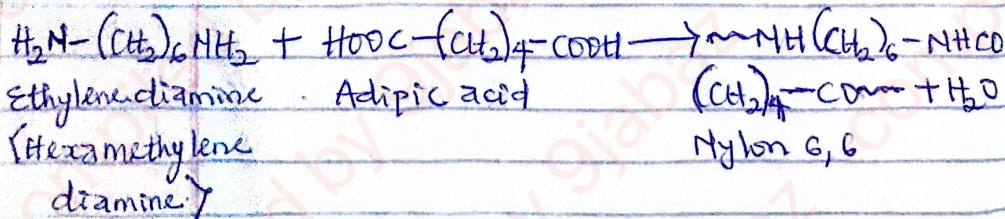
Another method of synthesis of block polymers occurs if polystyrene containing carboxylic acid groups is reacted

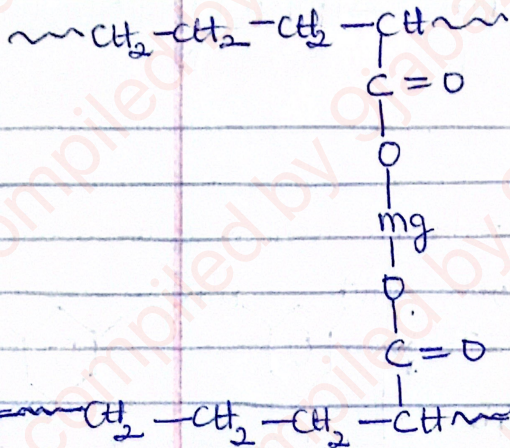
with ethylene glycol adipic acid condensation product yielding a block copolymer according to the following scheme



A block polymer.

Step copolymerization: Step of copolymerization condensation can be utilized in the synthesis of such products like polyamides and polyesters. The properties of these polymers differ according to the reactant used in the condensation reaction, e.g. Nylon 6,6 and Nylon 6,10 which can be produced by the reaction of Hexamethylene diamine and adipic acid or sebacic acid respectively. The Nylon 6,10 is more flexible and more moisture resistance than Nylon 6,6 on account of the longer hydrocarbon chain in the former. The following are examples of some steps co-polymer.





(An Ionomer)

Ionomers are thermoplastics at ^{high} ambient temperature and thermosets at ambient temperature.

② Styrene copolymer

- (i) Styrene-butadiene copolymer
- (ii) Styrene-acrylonitrile copolymer
- (iii) A B S Copolymer
 - Acrylonitrile
 - Butadiene
 - Styrene

③ Vinyl chloride copolymer

- (i) Vinyl chloride-vinyl acetate copolymer
- (ii) Vinyl chloride-vinylidene chloride copolymer

Elastomers / Elastomeric materials

Elastomers are rubber or rubber-like materials which possess definite elastic properties i.e. ability to undergo deformation on the application of force and then ^{regain} ~~again~~ the original

shape on removing the force. Examples of elastomers are;

- ① Polybutadiene
- ② Natural rubber (NR)
- ③ ~~Buta~~ Styrene butadiene rubber (SBR)
- ④ Butadiene rubber
- ⑤ Nitrile rubber
- ⑥ Chloroprene rubber etc

Some of the requirement of elastomers are;

- ① It should have high polymer
- ② It must be cross-linked and amorphous ~~crystalline~~
- ③ It should have flexibility of chain

Properties of Elastomers

- 1) Elastomers have weak intermolecular forces which allow them to stretch extensively
- 2) They are very flexible at low temperature
- 3) Their specific working temperature varies depending on their media compatibility
- 4) They have high viscosities which cause them to flow when force

24th = May 2024

Raw Rubber \Rightarrow Synthetic rubber

Rubber occurs in many tropical plants with the formula C_5H_8 .

It's commercial supply comes entirely from tree Heave *Brasilliensis* likely cultivated in plantation.

When an incision is made through the outer bark part of a rubber tree a milky fluid called the latex oozes out. It is colloidal suspension of rubber particle in water, addition of dilute acetic acid or formic acid

Causes coagulation of rubber in a cheese-like mass. ^{In} One

Common commercial process this mass is placed through rollers, washing with water to produce thin kinky sheets of light coloured pale crape rubber. In another process it is milled into thin sheet and smoked to get amber smoked rubber sheet. These two forms of rubber contains 95% of rubber hydrocarbons. The rubber hydrocarbon is often called caoutchouc. ^{A term} derived from the southern American ^{west} ~~words~~ ^{words} caa (for tears) and ochu (for wood) thus meaning tears of wood

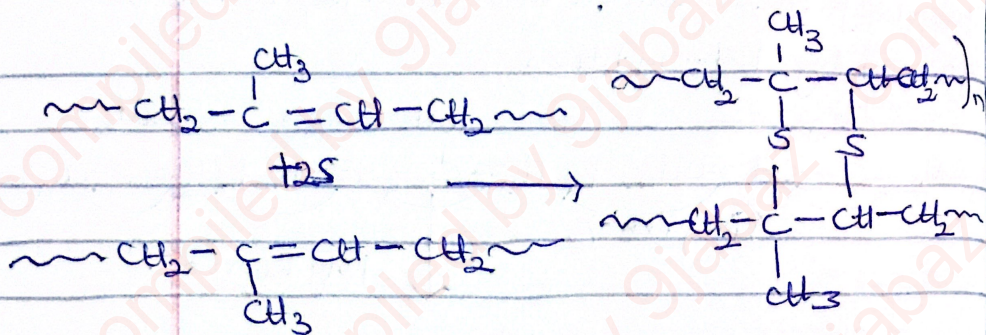
STRUCTURE OF RUBBER MOLECULE

Many workers have contributed to the unravelling of the structure of rubber molecules. On destructive distillation of rubber will produce Isoprene (C_5H_8) and dipentene ($C_{10}H_{16}$) were obtained. Analysis of rubber revealed that its empirical formula is $(C_5H_8)_n$. It is an unsaturated compound and has bromine, ^{chlorine} ~~fluorine~~ & hydrogen halides ^{when a}

It was found by pummerer that, dilute solvent of rubber in a solvent was hydrogenated in a presence of a catalyst, it yields a saturated compound $(C_5H_{10})_n$. On determining the molecular weight of rubber, the following data were obtained:

Osmotic pressure (number average) $7180,000 \text{ g mol}^{-1}$
viscosity $129,000 \text{ g mol}^{-1}$
Molecular weight by ultra centrifuge $400,000 \text{ g/mol}$

addition of $-Cl$ groups to the double bonds.



The vulcanization process is slow and found out that it could be accelerated & vulcanized and the vulcanized product of the superior ^{properties} ~~product~~ could be obtained. Example of such accelerator zinc;

- (i) phenyl methyl dithio carbamic acid
- (ii) Zinc dimethyl dithio carbamide. (ZnO)

A reinforcing agent like zinc oxide is used to obtain light-coloured stocks and carbon black for the production of tyre material. The vulcanized rubber thus produced still contain ~~unsaturation~~ in order to ^{protect} ~~product~~ rubber from unsaturation use of anti-oxidant was introduced. The highest anti-oxidant which led to superior which helps to reduce ageing performance of the finished product were aryl amines, diphenyl amines was one of the earliest anti-oxidant to be developed commercially but it was found to be too volatile to be used in modern

Rubber technology but later the higher molecular derivatives such as ~~oxidized~~ ^{oxygenated} diphenyl amines were found to be commercially suitable antioxidant for rubber & could be used at high temperature

Question

What do you understand by the term

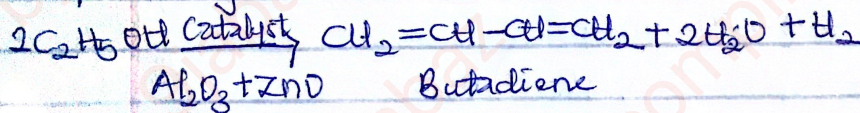
- i) Raw rubber
- ii) Vulcanized rubber
- iii) Anti-oxidant
- iv) Accelerator

Forms of Elastomers.

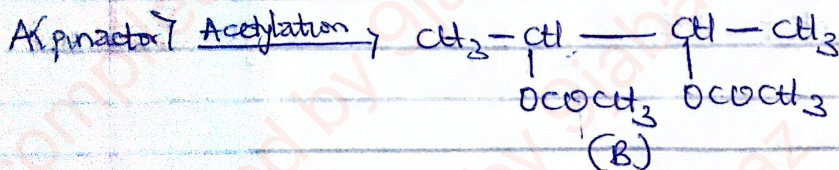
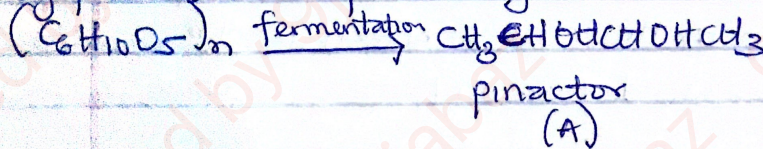
Buna rubbers.

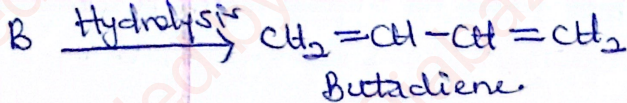
Buna rubbers are based on butadiene. The name buna was assigned since originally these rubbers were produced by the rxn of sodium on butadiene. Butadiene can be prepared as follows;

(i) From ethyl alcohol



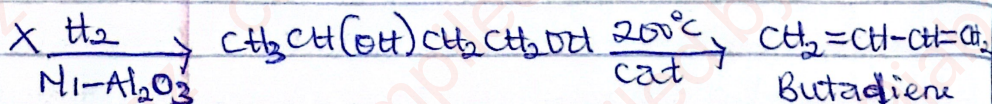
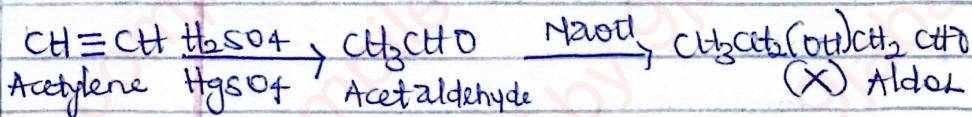
(ii) By fermentation of carbohydrates.





* With the aid of equations only describe the various routes of preparation of butadiene

1) from acetylene (ethyne)



Types of Buna rubbers.

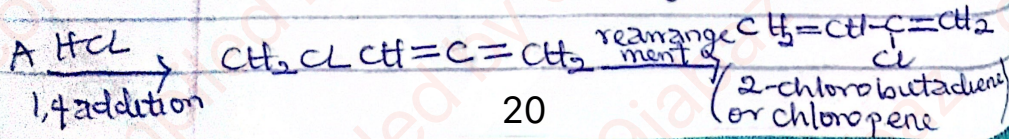
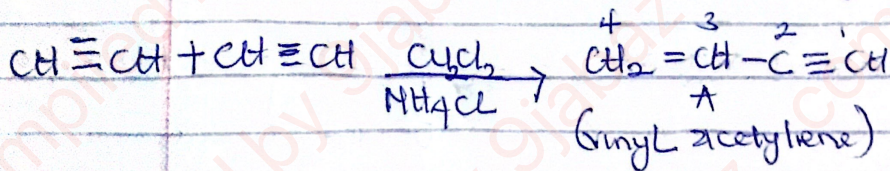
1) Buna 85 and Buna 115 (Industrial naming)

2) Buna (SBR, GRs) rubber

3) Buna-N (perbunan, GR-N) Rubber

Neoprene Rubber

The monomer in this case is known as chloroprene and can be synthesized from acetylene by the following steps:

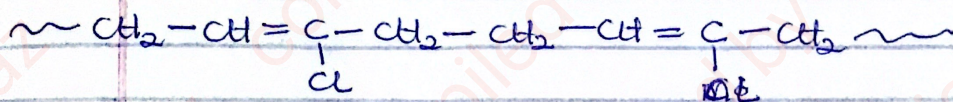


SBR Styrene butadiene rubber

G.R.S → Government regulated styrene

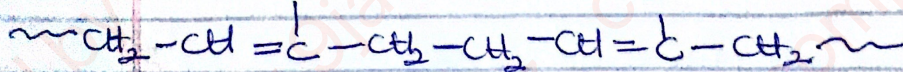
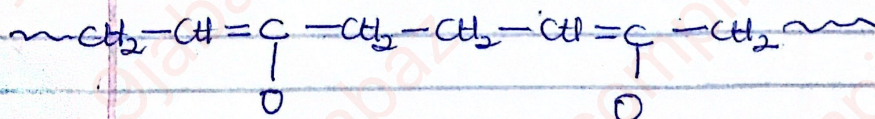
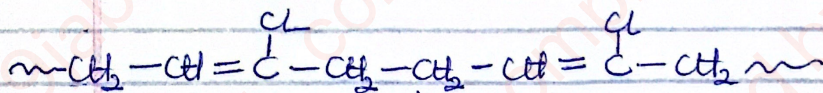
Polymerization of chloroprene

Polymerization of chloroprene takes place steadily and no catalyst is required, however it is very slow in the absence of oxygen. Vulcanization ^{of chloroprene} takes place in the ^{presence} of magnesium oxide & the following is the possible mechanism



+ MgO

+ MgO

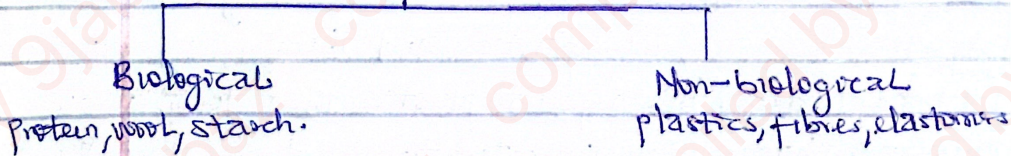


Vulcanization

PLASTICS

Macromolecules can be divided into biological and non-biological (synthetic). Examples of biological polymers are cellulose. Non-biological polymers are primarily synthetic materials used for plastics, fibres & elastomers. Though, few naturally occurring materials such as wool, rubber and cellulose are included in ^{non-}biological part because they can also be synthesized to make something useful.

Polymers



Plastics are used to refer to a wide range of semi-synthetic or synthetic organic polymers. *Semi-synthetic is talking of incorporating naturally occurring materials in a process to produce a material. There are different types of plastics known to possess physical and chemical properties. What makes different types of plastics to have different properties is because of what they are made of like their monomer composition, arrangement, structural formula etc. In short, the physical and chemical properties can categorize what type of plastic it is.

Some properties of plastics

- ⇒ light in weight and are chemically stable
- ⇒ plastics can be easily molded into different shapes and sizes
- It may require, the addition of additives like plasticisers such as adipates, azelates, citrates, phthalates etc.
- ⇒ plastics are good insulators. They possess good insulation and low thermal conductivities.
- ⇒ plastics are resistant to corrosion
- ⇒ They possess poor dimensional stability and can be easily deformed.
- ⇒ For any commercial purpose, they should have low processing cost.

Plastics can be divided into two broad types because of its properties. They are, thermoplastics and thermosetting plastics.

Thermoplastics: This refers to plastics that do not undergo any chemical changes when subjected to high temperature. These plastics do not undergo any changes in their chemical structure and chemical compositions when subjected to heat and can be changed into a soft state and remoulded multiple times.
eg polystyrene, nylon etc

Thermosetting plastics: are as well known as thermosets. They are plastics that can be moulded only once and not change shape on application of heat. They can not be softened on further application of heat instead they will get burnt up eg car tyres. They undergo degradation and become damaged when exposed to a large amount of heat eg vulcanized rubbers, epoxy resins, polyurethane

All plastics are polymers but not all polymers are necessarily plastics. Polymers are not precisely macromolecules because polymers are composed of repeating unit whereas macromolecules may not be composed of repeating units.

What is a polymer? A polymer is a large molecule built up by the repetition of small chemical unit referred to as repeating units which are held together by chemical covalent bonds. The repeating units are generally referred to as monomers.

Polymers do not have uniform composition

In some cases, the repeating units (repetition of monomers) is linear. In other cases, you can have branched chain polymers. The repeating unit of the polymers are usually / nearly equivalent to the monomers or the starting materials from which the polymer is formed.

Polymers are macromolecules

Macromolecules are large molecules. * plastics are polymers but polymers are not plastics because plastics is not the only polymer.

Nylon are plastics. plastics does not necessarily have to be brittle or very hard. Satchet of water is also a plastic. Nylon is

Just a specific name. 2 molecules of molecules {Dimer}

More than 3 molecules of monomer \Rightarrow polymer.

$\Delta P = \text{Degree of polymerization}$

22nd May 2024

polymer is the degree of polymerization. Degree of polymerization is the molecular weight of the polymer divided by the molecular weight of repeating unit / monomer

$\Delta P = \frac{\text{Molecular weight of polymer}}{\text{Molecular weight of repeating unit (monomer)}}$

Molecular weight of repeating unit (monomer)

The degree of polymerization is the number of repeating unit or monomer on the chains of the polymer. The molecular weight of the addition polymer is the product of the repeating unit & the degree of polymerization

M.Wt of polymer = $\Delta P \times$ molecular wt of a monomer.

Classification of polymers

We can classify polymer based on their mechanical strength & behaviour. Eg low density poly^{ethylene} & high density poly^{ethylene}

2) By the process of production: the process will affect the product.

3) Their molecular arrangement.

It affect the ppts & type of polymer you can have

4) The type of monomer involved in the polymer.

5) The morphology of the polymeric substance. The kind of polymer produced. polymer can also be classified based on natural sources and synthetic resources. Eg of natural ^{will also affect} occurring polymer is rubber

other factors such as Natural & Synthetic source
Comparison of Thermoset & Thermoplastic polymer

Thermoplastic: They are usually formed by addition polymerization leading to long linear chain polymer with no cross-link. (2) They are usually readily softened when exposed to high temperature because secondary forces btw the individual chains can break easily by heat, light or pressure.

3) They can be reshaped & ~~re-used~~ re-used from waste.

Thermoplastic can melt & assume shape of the container which is being put so therefore, you can reshape it.

4) They are usually soft, weak & less brittle because they are not crystalline in nature. Eg polypropylene, PVC, polystyrene, nylon etc

Thermosets: They are usually formed by condensation polymerization with three dimensional network structures i.e they are cross linked. Eg Tyre

1) They do not soften when subjected to high temperature or heat & ~~prolong~~ ^{prolong} exposure to high temperature it result in ~~burning~~ ^{charring} of the polymers.

2) They cannot be reshaped or re-used

3) They are usually, hard strong & brittle

4) Thermosets cannot be reclaimed from waste due to strong bonds having inter & intra chain cross linking. They are ⁽⁶⁾ insoluble in almost all organic solvents.

Eg Epoxiresin, Silicose, bakilite

Natural Polymers

These are polymers obtained from plant & animal origin e.g cellulose, starch, protein, wool, silk, leather

Synthetic Polymers

They are synthetically produced or prepared in the laboratory.

Homopolymers and Co-polymers:

Homopolymers are formed from a single monomer unit such as $[AAAAAA]$ $[BBBBBB]$

Co-polymers are polymeric compounds which are built up of two different types of monomeric unit in their chain. They can as well be called mixed polymer. Polymers with three different types of non-numeric unit are referred to as ter-polymers. Sometimes, they are not arranged in a particular order. Co-polymer can be further classified into;

1) Alternating co-polymers or

statistically regular copolymer such as having the repeating unit Eg $ABABABAB$

2) Random copolymer or statistically irregular copolymer.

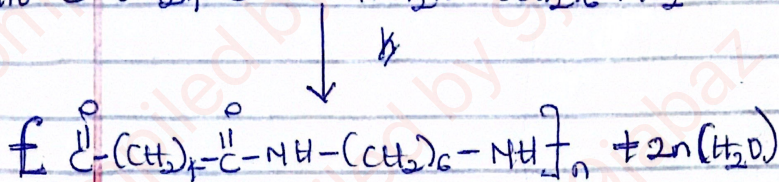
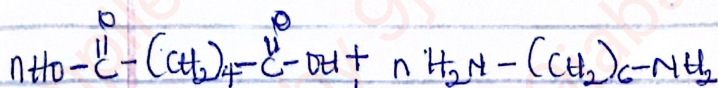
In alternating copolymer both repeating polymer or monomer are joined side to side.

For Random or Irregular copolymer no regular joining of ^{two} or more monomer. Eg $ABBAAABAB$

No regular pattern, it is just mixed.

Adipic acid

hexamethylenediamine



Nylon 6-6

29th May 2024

ORGANIC POLYMERS

Organic polymers are polymers whose back bond chain are essentially made of carbon atoms. The atoms attached to the side valencies of the back bone atoms are usually carbon, nitrogen, hydrogen and halogens, oxygen. For this polymer, the number and varieties are so large to the extent that usually, they form under the aliphatic and aromatic carbon which can be further classified as homo chain and heterochain.

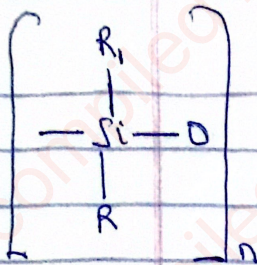
Homo chain \Rightarrow Polyethylene, polybutadiene, pvc etc

Element of Organic polymer:

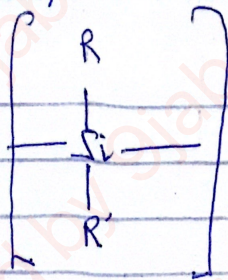
They are compounds whose chains are composed of carbon atoms, heteroatoms, excluding N, S and O. In this particular polymer, we have compound with inorganic chains with side groups attached to the chains

Attached to the groups are carbon atoms that can be indirectly connected to the backbone. They are compounds whose main chain contains carbon atoms and side groups contains

hetero atoms except N, S and, O and halogens.

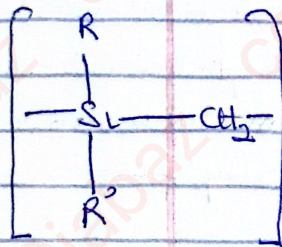


silicone

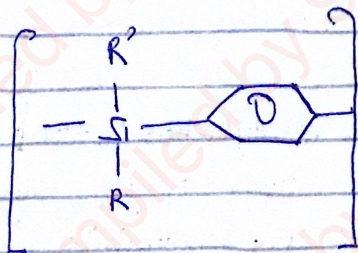


no heteroatoms.

{ poly siloxanes }



polycarbon-silanes

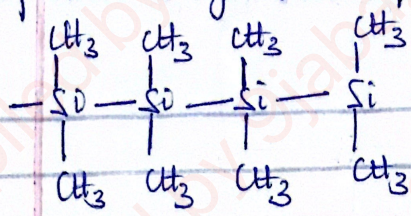


poly sphenylenes.

Inorganic polymers.

These are polymers containing no carbon but could have Si-Si, Si-O, N-P, B-O linkages in the polymer. Examples are polysilanes, polyphosphoric acid. These polymers types possess superior thermal, electrical and mechanical properties over the organic polymers. They are always stronger than the organic polymers. The polymer contains elements from group 4 to group 6 on the periodic table. Elements of group 4 can form linear polymers. Polymers formed by element of group 5 are usually of low molecular weight while the polymers formed by elements of group 6, especially with sulphur and selenium

Usually have a high tendency to form homo-chain

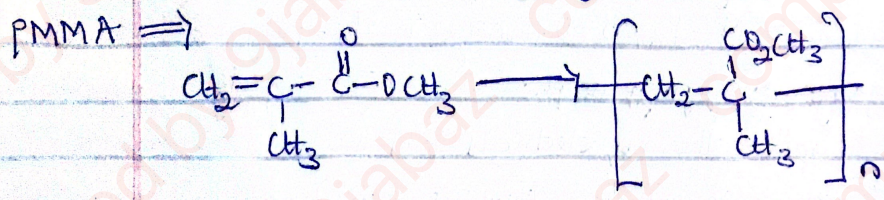
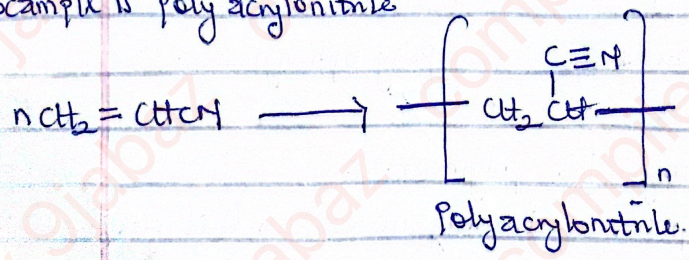


Polysilanes

30th May 2024

ADDITION POLYMER

They are usually linear or branched polymer with little or no cross linking. As a result, they are thermoplastic materials which flow easily when heated and can be moulded into variety of shapes. Acrylic polymers are usually fibres. An example is polyacrylonitrile



Poly(methyl methacrylate)

Condensation polymer. These are synthetic polymer consisting of more than one or more monomer.

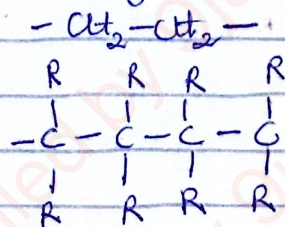
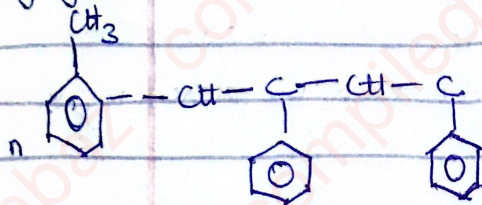
Characteristics that define a polymer

* Tacticity of polymer: This is the arrangement/organization

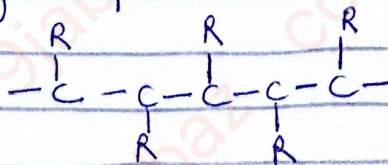
of dependent groups around the backbone of a polymer. It is an important characteristic that defines polymer classification according to tacticity.

i) Isotactic polymer (ii) Syndiotactic polymer (iii) Atactic polymer.

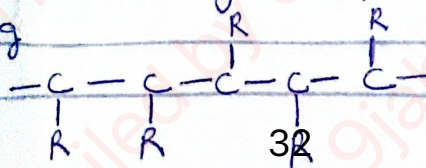
Isotactic polymer: are polymers consisting of chain segment which display a regular repetition of the monomer unit with the carbon atoms of the backbone of the polymer. It can be polystyrene.



Syndiotactic polymers: The chains consist of regular species of monomers in which even second atoms of the chain possess opposed steric configuration which means they have regularity on the substituent of the polymer chain. E.g.



Atactic polymer: Their chains lack regularity in the distribution of the steric configuration of the monomer unit. So there is random arrangement of substituent on the polymer chain. E.g.



Classification according to crystallinity.

1) Amorphous polymers: They are glassy in nature. They are non-crystalline polymers that have no element of crystallinity in them. They are clear.

2) Crystalline polymers: They are usually translucent. They have ~~highly~~ highly regions in the polymer and some amount of amorphous in the structure. No polymer is 100% crystalline.

Thermoset: crosslink

Thermoplastics: no crosslink

Branched polymers are less dense than linear polymer because they have the opportunity to be packed together.