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Maharashtra Institute of Technology, Aurangabad

Department of Plastic and Polymer Engineering

LABORATORY MANUAL

ACADEMIC YEAR: 2019-20 PART: I
COURSE: Polymer Synthesis-II COURSE CO-ORDINATOR: Ms. J.S.Suryawanshi

Experiment No.-1

Aim: Synthesis of Novolac resin**.**

Apparatus:

3 Neck flask / Resin reaction flask, mechanical stirrer, thermometer jacket, Dropping funnel with pressure equalizer, condenser, thermometer, water, heating mantle, funnel, dropper, measuring cylinder, rubber tube for water, glass rod , PP petridis, glass petridis (Large) etc.

Chemicals:

Phenol, Formalin/37% formaldehyde, Oxalic Acid/H_2SO_4,

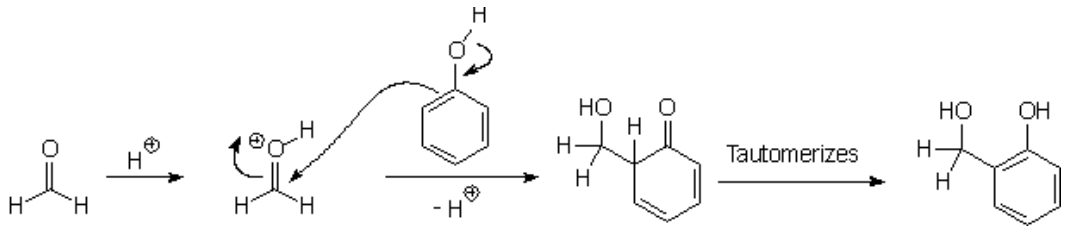
Theory:

Novolac is a type of Phenol formaldehyde resin or P-F resin or phenolic resins (also called phenoplasts). Such polymers are formed by condensation polymerization of phenol and formaldehyde in acidic medium.

Mechanism:

The reaction between phenol and formaldehyde was a condensation reaction in which water was liberated as a byproduct. Phenol and Formaldehyde reacts in a molar ratio 1:0.8 under acidic condition yields mononuclear monomethylol phenols as shown in step (i). In step (ii), the mononuclear products react with the phenol and other monomethylol phenols to obtain binuclear product. In the subsequent steps, it polymerizes to form linear novolac resin as shown in (iii). Such type of material does not cure on heating. An additional additive (Mainly Hexamethylene tetraamine) is used to cure the material to form thermoset resin. Novolac is generally soluble and fusible material.

(i)



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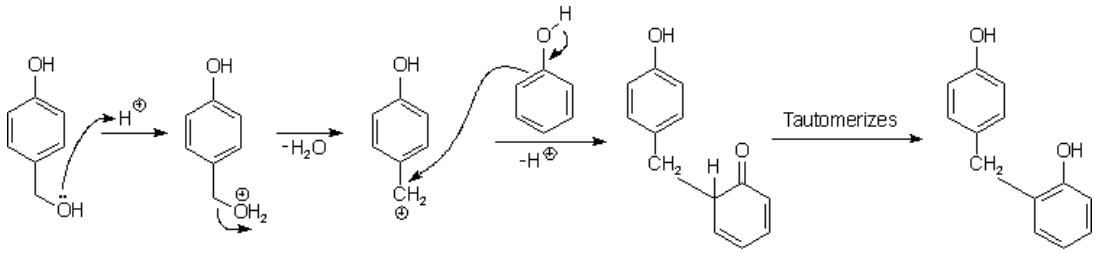
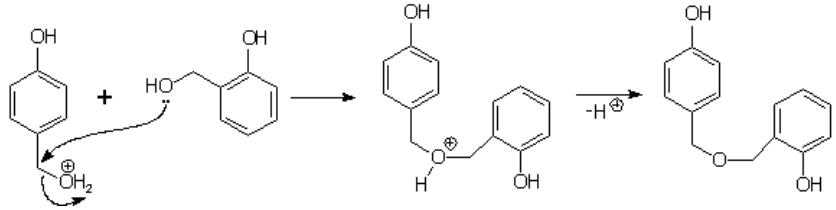
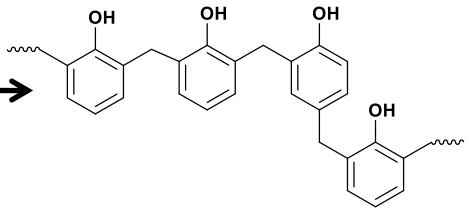
(ii)



(iii)



(iv) **(i) + (ii) + (iii)** ⟶



Procedure:

1. A 3 necked flask is taken and fitted with condenser, stirrer, dropping funnel and inlet for nitrogen gas.

2. Then assembly is kept in a water bath and heated to 65-75^{o}C.

3. Calculate the amount of phenol and formaldehyde required to obtain 250 gm. of Novolac resin.

4. The required amount of phenol is first taken in the flask.

5. Heat it to 65-70^{o}C.

6. Required amount of formaldehyde solution is added to the phenol.

7. Then oxalic acid is taken of the amount of 1.6 weight percent of the weight of phenol taken and added to the aliquot under stirring condition.

8. The reaction mixture is stirred for about two hour and the temperature was maintained at 75^{o}C.

9. As required viscosity is achieved the solution is cast on a PP Petridish and allowed to cool.

10. The resin is then washed with water to remove acid catalyst or any other unreacted materials. The product is then sintered in oven at 80 ˚C.

Calculation of weight of the reactants:

Assumption: Let us assume that X moles of phenol are required to prepare 250 gm. of Novolac.

Reaction:	C_6H_5OH + 0.8 HCHO	⟶	Novolac + H_2O	
Molecular Weight:	94	30		18
Moles:	1	0.8		0.8
Weight (gm.):	94	(30 *0.8)=24	(18*0.8)=14.4	
For X moles weight (gm.):	**94X**	**24X**	**250**	**14.4X**

Overall material balance: 94X+24X=250+14.4X

X = 2.413 moles

Therefore, weight of phenol required = $\frac{94 \times X \times 100}{\%\ of\ purity}$ gm.

Characterization:

(i) **Weight of the PP Petridis =** …… gm. (A)

(ii) **Weight of the PP Petridis + Product =** ……. gm. (B)

(iii) **Yield (%) =** $\frac{(B-A)\times 100}{250}$

(iv) **Solubility:** One gm. of the sample is taken in a beaker and 20 ml of the solvent is added to it.

Water	Dimethyl formamide	Tetrahydrofuran	Acetone	Toluene

(v) **Viscosity:** Solution viscosity is measured by taking solution of the resin in DMF (15 ml) using Ubbhelohde Viscometer.

Temperature = ……. ˚C

Density of toluene (ρ)= …….. gm./c.c.

$T_{toluene}$ = ……. Sec.

$T_{solution}$ = ……. Sec.

Specific Viscosity (η_{sp})= ($T_{solution}$ - $T_{toluene}$)/ $T_{toluene}$ =

Reduced Viscosity (η_{red})= η_{sp}/concentration of solution =

Inherent viscosity (η_{inh}) = ln η_{red}/ C

Determination of intrinsic viscosity: Reduced viscosity is plotted against concentration of the solution using linear fitting. Extrapolation of the linear fitted curve to Y axis provides the value of intrinsic viscosity.

Determination of molecular weight: Viscosity average molecular weight is determined using Mark-Houwink equation, $[\eta] = K M^{\alpha}$. Here K and α is Mark-Houwink parameters.

$K = 1.80 \times 10^{-3}$

$\alpha = 0.51$

$\overline{M_V}$ =

(vi) **Formalin Content:**

Theory: Hydroxylamine hydrochloride reacts with free formaldehydes present in the sample and liberates HCl which is titrated against sodium hydroxide using bromophenol blue indicator.

Procedure:

(1) 0.1 (N) NaOH solution is prepared qualitatively in a 500 ml stoppered conical flask by dissolving 1.6 gm of NaOH in 400 ml of distilled water.

(2) 0.1 (N) Oxalic acid is prepared in a 100 ml. volumetric flask by accurately weighing 0.63 gm. in the said flask and make up the rest of volume with distilled water.

(3) Standardization of sodium hydroxide solution is performed by titrating it with 10 ml of oxalic acid solution (Primary Standard) using phenolphthalein indicator/Universal indicator.

(4) About 5 gm. of sample resin is weighed and dissolved in 10 ml of hydroxylamine hydrochloride in 100 ml conical flask.

(5) The mixture is then titrated under stirring condition against 0.1(N) sodium hydroxide using bromophenol blue indicator.

(6) Blank titration is carried out under identical condition using only 10 ml of hydroxylamine hydrochloride. end point is yellow to light violet.

[**Note**:

(i) Sodium hydroxide solution should be taken in burette

(ii) End point is detected by color change from colorless to pink (basic) for phenolphthalein indicator and yellow to light violet for bromophenol blue indicator.

(iii) After titration wash the burette thoroughly with water to remove sodium hydroxide from the burette. Then it should be rinsed several times with acetone before leave the room.]

Applications:

Assignment: 1. How Novolac is prepared?

2. Explain the reaction between phenol and formaldehyde and the process of forming Novolac resin.

3. Write down the properties and possible applications of Novolac.

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ACADEMIC YEAR: 2019-20 PART: I
COURSE: Polymer Synthesis-II COURSE CO-ORDINATOR: Ms. J.S.Suryawanshi

Experiment No.-2

Aim: Synthesis of Resol resin**.**

Apparatus:

3 Neck flask / Resin reaction flask, mechanical stirrer, thermometer jacket, Dropping funnel with pressure equalizer, condenser, thermometer, water, heating mantle, funnel, dropper, measuring cylinder, rubber tube for water, glass rod , PP petridish, glass petridish (Large) etc.

Chemicals:

Phenol, Formalin/37% formaldehyde, Sodium hydroxide.

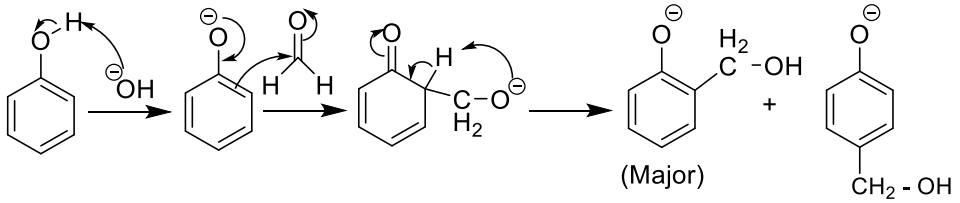
Theory:

Resol is a type of Phenol formaldehyde resin or P-F resin or phenolic resins (also called phenoplasts). Such polymers are formed by condensation polymerization of phenol and formaldehyde in basic medium. The molar ratio of phenol to formaldehyde was 1:2.

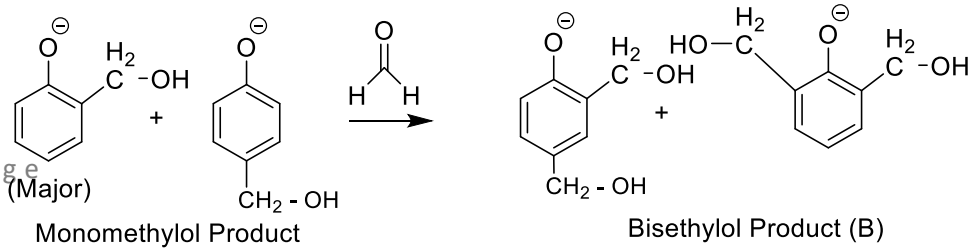
Mechanism:

The reaction between phenol and formaldehyde was a condensation reaction in which water was liberated as a byproduct. Phenol and Formaldehyde reacts in a molar ratio 1:2 under basic condition which yields a mixture of mononuclear monomethylol and bismethylol phenols as shown in step (i) and (ii).

(i)



(ii)



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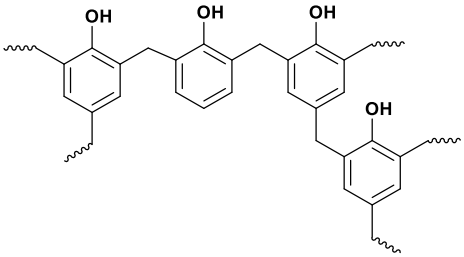
(iii) A + B ⟶ 

The Product is then polymerized under identical condition as shown in step (iii).

Procedure:

1. A 3 necked flask is taken and fitted with condenser, stirrer, dropping funnel and inlet for nitrogen gas.

2. Then assembly is kept in a water bath and heated to 70^{o}C.

3. Calculate the amount of phenol and formaldehyde required to obtain 250 gm. of Resol resin.

4. The required amount of phenol is first taken in the flask.

5. Heat it to 70^{o}C.

6. Required amount of formaldehyde solution is added to the phenol.

7. Then sodium hydroxide is taken of the amount of 1 weight percent of the weight of phenol taken and added to the aliquot under stirring condition.

8. The reaction mixture is stirred for about two hour and the temperature was maintained at 75^{o}C.

9. When two layer are phase separated then the stirring is stopped.

10. Sulphuric acid is added to decrease the pH and it is kept at 6-7.

11. The temperature should not increase more than 70 C.

12. The product is removed and cast on PP petridish. The product is called as resin A.

13. The byproduct water liberated during the reaction is collected through Dean- Stark apparatus and measured using a measuring cylinder.

14. If the reaction is continued after that then resin C is obtained which is insoluble and infusible residue.

15. The product is then sintered in oven at 80 ˚C.

Calculation of weight of the reactants:

Assumption: Let us assume that X moles of phenol are required to prepare 250 gm. of Resol.

Reaction:	C_6H_5OH + 1.2 HCHO	⟶	Resol + H_2O	
Molecular Weight:	94	30	18	
Moles:	1	1.2	1.2	
Weight (gm.):	94	(30 *1.2)=36	(18*1.2)=21.6	
For X moles weight (gm.):	**94X**	**36X**	**250**	**21.6X**

Overall material balance: 94X+36X=250+21.6X

X = 2.306 moles

Therefore, weight of phenol required = $\frac{94 \times X \times 100}{\%\ of\ purity}$ gm.

Characterization:

(i) **Weight of the PP Petridis =** …… gm. (A)

(ii) **Weight of the PP Petridis + Product =** ……. gm. (B)

(iii) **Yield (%) =** $\frac{(B-A)\times 100}{250}$

(iv) **Solubility:** One gm. of the sample is taken in a beaker and 20 ml of the solvent is added to it.

Water	Dimethyl formamide	Tetrahydrofuran	Acetone	Toluene

(v) **Viscosity:** Solution viscosity is measured by taking solution of the resin in DMF (15 ml) using Ubbhelohde Viscometer.

Temperature = ……. ˚C

Density of toluene (ρ)= …….. gm./c.c.

$T_{toluene}$ = …… Sec.

$T_{solution}$ = …… Sec.

Specific Viscosity (η_{sp})= ($T_{solution}$ - $T_{toluene}$)/ $T_{toluene}$ =

Reduced Viscosity (η_{red})= η_{sp}/concentration of solution =

Inherent viscosity (η_{inh}) = ln η_{red}/ C

Determination of intrinsic viscosity: Reduced viscosity is plotted against concentration of the solution using linear fitting. Extrapolation of the linear fitted curve to Y axis provides the value of intrinsic viscosity.

Determination of molecular weight: Viscosity average molecular weight is determined using Mark-Houwink equation, $[\eta] = K M^{\alpha}$. Here K and α is Mark-Houwink parameters.

$K = 1.80 \times 10^{-3}$

$\alpha = 0.51$

$\overline{M_V}$ =

(vi) **Formalin Content:**

Theory: Hydroxylamine hydrochloride reacts with free formaldehydes present in the sample and liberates HCl which is titrated against sodium hydroxide using bromophenol blue indicator.

Procedure:

(1) 0.1 (N) NaOH solution is prepared qualitatively in a 500 ml stoppered conical flask by dissolving 1.6 gm of NaOH in 400 ml of distilled water.

(2) 0.1 (N) Oxalic acid is prepared in a 100 ml. volumetric flask by accurately weighing 0.63 gm. in the said flask and make up the rest of volume with distilled water.

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(3) Standardization of sodium hydroxide solution is performed by titrating it with 10 ml of oxalic acid solution (Primary Standard) using phenolphthalein indicator/Universal indicator.

(4) About 5 gm. of sample resin is weighed and dissolved in 10 ml of hydroxylamine hydrochloride in 100 ml conical flask.

(5) The mixture is then titrated under stirring condition against 0.1(N) sodium hydroxide using bromophenol blue indicator.

(6) Blank titration is carried out under identical condition using only 10 ml of hydroxylamine hydrochloride. end point is yellow to light violet.

[**Note**:

(i) Sodium hydroxide solution should be taken in burette

(ii) End point is detected by color change from colorless to pink (basic) for phenolphthalein indicator and yellow to light violet for bromophenol blue indicator.

(iii) After titration wash the burette thoroughly with water to remove sodium hydroxide from the burette. Then it should be rinsed several times with acetone before leave the room.]

Applications:

Assignment: 1. How Resol is prepared?
2. Explain the reaction between phenol and formaldehyde and the process of forming Resol resin.
3. Write down the properties and possible applications of Resol.
4. Write down the differences in properties between Novolac and Resol.

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ACADEMIC YEAR: 2019-20 PART: I
COURSE: Polymer Synthesis-II COURSE CO-ORDINATOR: Ms. J.S.Suryawanshi

Experiment No. - 3

Aim: Synthesis of Urea Formaldehyde Resin.

Apparatus:

3 Neck flask, mechanical stirrer, thermometer jacket, Dropping funnel with pressure equalizer, condenser, thermometer, water, heating mantle, funnel, dropper, measuring cylinder, rubber tube for water, glass rod , PP petridis, glass petridis (Large) etc.

Chemicals:

Urea, Formalin, Sodium hydroxide (2N), Liquid Ammonia

Theory: Urea Formaldehyde resin is a type of amino resin which comprises about 80% of the market of amino resin produced globally. Amino resin are the condensation product obtained by the reaction of formaldehyde and nitrogen containing monomers such as urea, melamine, aniline etc. The molar ratio of urea to formaldehyde is generally taken as 1:1.5 to 1:1.8 to obtain urea-formaldehyde resin. Advantage of urea-formaldehyde resin includes – (i) low cost, (ii) Easy applicability, (iii) low cure temperature, (iv) water solubility, (v) Resistance to microorganisms, (vi) High abrasion resistance, (vii) Excellent hardness, (viii) Excellent thermal properties, (ix) low color generation during curing etc. Inspite of so many advantages the resin bears few disadvantages like – (i) Poor moisture barrier properties, (ii) Low acid or alkali resistance, (iii) hydrolytic degradation leads to evolve poisonous formaldehyde etc. Such lacunas restrict its use to interior purposes.

Mechanism:

Urea-formaldehyde resins are formed by the condensation reaction of urea and formaldehyde at a temperature of 50 – 80 ˚C. The synthesis of resin takes place in two stages.

(i) In the first stage, urea is hydroxymethylolated by the addition of formaldehyde to the amino groups under basic condition (pH = 8-9). The product is mono, di, and tri-methylol urea. Tetramethylol urea is apparently not produced in appreciable quantity during the reaction. This step is carried out under basic condition to suppress the condensation reaction among the methylol groups. Here, molar ratio of formaldehyde and urea is kept at nearly 2. The reaction temperature is maintained at 80 ˚C.

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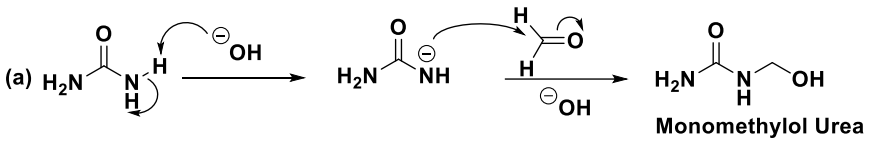
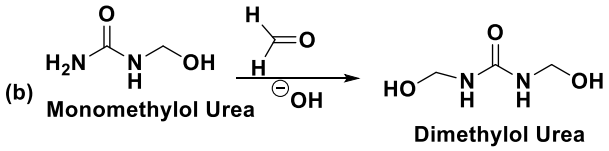
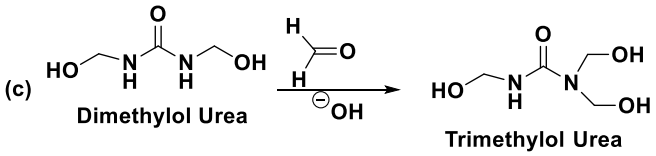
Stage I :

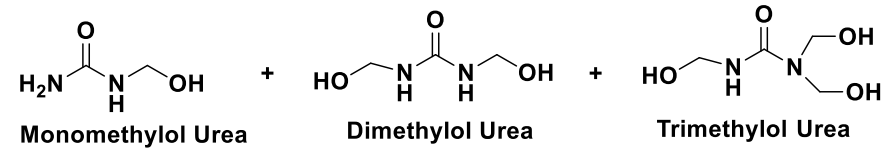


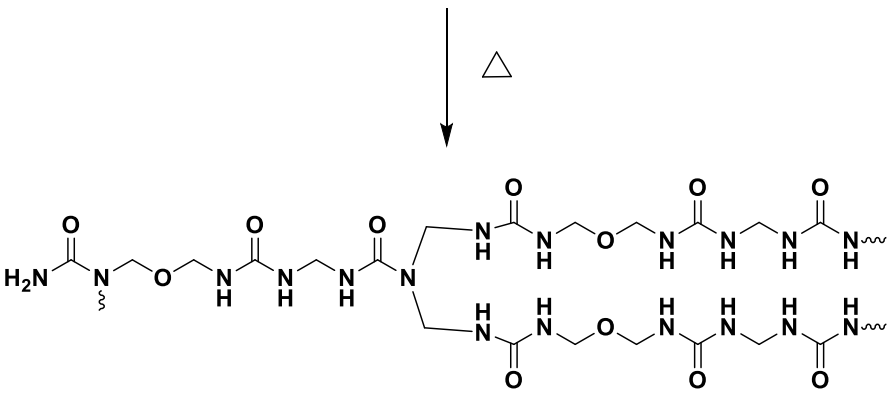




(ii) In the second step, the pH of the aliquot is brought to acidic region (PH <5). Here the urea is added to bring the molar ratio (formaldehyde : urea) to 1.5 to 1.8. The urea is added at a temperature of 45 ˚C to maintain the desired formaldehyde : urea.

Stage II :





Urea Formaldehyde resin

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Curing of resin: The resin is acid cured where mostly ammonium chloride and ammonium sulphate are used. Such catalysts are used as it reacts with the unreacted formaldehyde which results in lowering the formaldehyde content in the resin at the time of curing of the resin. Except them, other acid catalysts like formic acid, boric acid, phosphoric acid, oxalic acid, and acid salts of hexamethylenetetramine etc. Resin cure is normally conducted a a temperature of ~120 ˚C and a pH < 5.

Procedure:

1. The required amount of formalin was first taken in a beaker & then it was neutralized using sodium hydroxide solution in presence of phenolphthalein indicator to remove excess acid present i.e. formic acid.

2. It was then transferred to a 3 necked flask & stirred till 50 ˚C temp. is attained.

3. Then two third amount of total urea is added to the reaction mixture [Urea should be added in very small amount at a time as it results in exotherm] and after the addition the reaction is stirred at 80 ˚C.

4. The reaction temperature is decreased to 45 ˚C.

5. The pH of the reaction medium is increased to 8 by adding ammonium catalyst and the rest of the urea is added in 2 parts at a 10 minutes interval. [After addition of urea, there was slight increase in exothermic dissipation]

6. The reaction is allowed to continue for 20 minutes after the last addition of urea and the reaction temperature is maintained at 60 to 70 ˚C.

7. & ammonia catalyst was added into reaction flask & then the whole mixture was continuously stirred & temp. 60^0C-70^0C was maintained.

8. The pH of the mixture is maintained at 7.5 - 8.

9.The reaction is stopped when the solid content is reached to about 40% and the mass is cast on a petridish.

Calculation of weight of the reactants:

Assumption: Let us assume that X moles of phenol are required to prepare 250 gm. of UF resin.

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Reaction: $(NH_2)_2C=O + 1.5\ HCHO \longrightarrow UF + H_2O$

Molecular Weight:	60.06	30	18
Moles:	1	1.5	1.5
Weight (gm.):	60.06	(30 *1.5)=45	(18*1.5)=27
For X moles weight (gm.):	**60.06X**	**45X**	**250 27X**

Overall material balance: 60.06X+45X=250+27X

X = 3.2027 moles

Therefore, weight of phenol required = $\frac{60.06 \times X \times 100}{\%\ of\ purity}$ gm. = …….. gm.

Weight of formaldehyde required = 45 X = 45 * 3.2027 = 144.12 gm.

Volume of formalin = 144.12/concentration of formalin ml. = …… ml.

Characterization:

(i) **Weight of the PP Petridis =** …… gm. (A)

(ii) **Weight of the PP Petridis + Product =** ……. gm. (B)

(iii) **Yield (%) =** $\frac{(B-A)\times 100}{250}$

(iv) **Solubility:** One gm. of the sample is taken in a beaker and 20 ml of the solvent is added to it.

Water	Acid	Alkali	Tetrahydrofuran	Acetone	Toluene

(v) Solid content: 1 gm. of the mixture is taken and dried in oven at 100 C. The weight is measure after the complete drying of the sample.
Weight of the petridish = …… gm (A)
Weight of PP Petridish + Product (Before drying) = ……. gm.(B)
Weight of PP Petridish + Product (After drying) = ……. gm. (C)

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Solid Content = $\frac{(C-A)}{(B-A)} \times 100$

(vi) Viscosity:

About 20ml of resin was taken in B ford cup viscometer keeping lower hole closed. It was then released & viscosity of resin was determined by using stopwatch. The procedure was repeated for 2-3 times till constant reading obtained.

(vii) Formalin Content:

Theory: Hydroxylamine hydrochloride reacts with free formaldehydes present in the sample and liberates HCl which is titrated against sodium hydroxide using bromophenol blue indicator.

Procedure:

(1) 0.1 (N) NaOH solution is prepared qualitatively in a 500 ml stoppered conical flask by dissolving 1.6 gm of NaOH in 400 ml of distilled water.

(2) 0.1 (N) Oxalic acid is prepared in a 100 ml. volumetric flask by accurately weighing 0.63 gm. in the said flask and make up the rest of volume with distilled water.

(3) Standardization of sodium hydroxide solution is performed by titrating it with 10 ml of oxalic acid solution (Primary Standard) using phenolphthalein indicator/Universal indicator.

(4) About 5 gm. of sample resin is weighed and dissolved in 10 ml of hydroxylamine hydrochloride in 100 ml conical flask.

(5) The mixture is then titrated under stirring condition against 0.1(N) sodium hydroxide using bromophenol blue indicator.

(6) Blank titration is carried out under identical condition using only 10 ml of hydroxylamine hydrochloride. end point is yellow to light violet.

[**Note**:

(i) Sodium hydroxide solution should be taken in burette

(ii) End point is detected by color change from colorless to pink (basic) for phenolphthalein indicator and yellow to light violet for bromophenol blue indicator.

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(iii) After titration wash the burette thoroughly with water to remove sodium hydroxide from the burette. Then it should be rinsed several times with acetone before leave the room.]

Applications:

Assignment:

(i) Explain the different types of reactions involved in the production of UF resin.
(ii) Write a short note on the impact of pH and temperature of the reaction medium on the properties of urea-formaldehyde resin.
(iii) Write down few advantages and disadvantages of the resin.
(iv) Write briefly on the catalyst used for curing UF resin moulding compounds.
(v) How is excessive shrinkage prevented in UF resin moulding compounds.

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ACADEMIC YEAR: 2019-20 PART: I
COURSE: Polymer Synthesis-II COURSE CO-ORDINATOR: Ms. J.S.Suryawanshi

Experiment No. - 4

Aim: Synthesis of Melamine Formaldehyde Resin.

Apparatus:

3 Neck flask, mechanical stirrer, thermometer jacket, Dropping funnel with pressure equalizer, condenser, thermometer, water, heating mantle, funnel, dropper, measuring cylinder, rubber tube for water, glass rod , PP petridis, glass petridis (Large) etc.

Chemicals:

Melamine, Formalin, Sodium hydroxide (2N).

Theory: Melamine Formaldehyde resin is a type of amino resin which comprises about 20% of the market of amino resin produced globally. Amino resin are the condensation product obtained by the reaction of formaldehyde and nitrogen containing monomers such as urea, melamine, aniline etc. The molar ratio of Melamine to formaldehyde is generally taken as 1:3 to obtain melamine-formaldehyde resin. Advantage of urea-formaldehyde resin includes – (i) Excellent weathering resistance, (ii) Excellent colorability, (iii) High hardness, (iv) Exceptional arc resistance etc. In spite of so many advantages the resin bears few disadvantages like – (i) High cost, (ii) inferior acid or alkali resistance ability, (iii) Not microwave same as it tends to absorbs radiation and evolve poisonous elements. Such lacunas restrict its use. It is marketed under a variety of commercial names, including Saduren, Maprenal, Resimene, and Leaf.

Mechanism:

The MF resin is obtaing in two stages. In the first stage, the mixture of mono-methylol, dimethylol and tri-methylol derivative of melamine is obtained. Further continuation of heating results in condensation of methylol melamines. The polycondensation reaction leads to Melamine formaldehyde resin.

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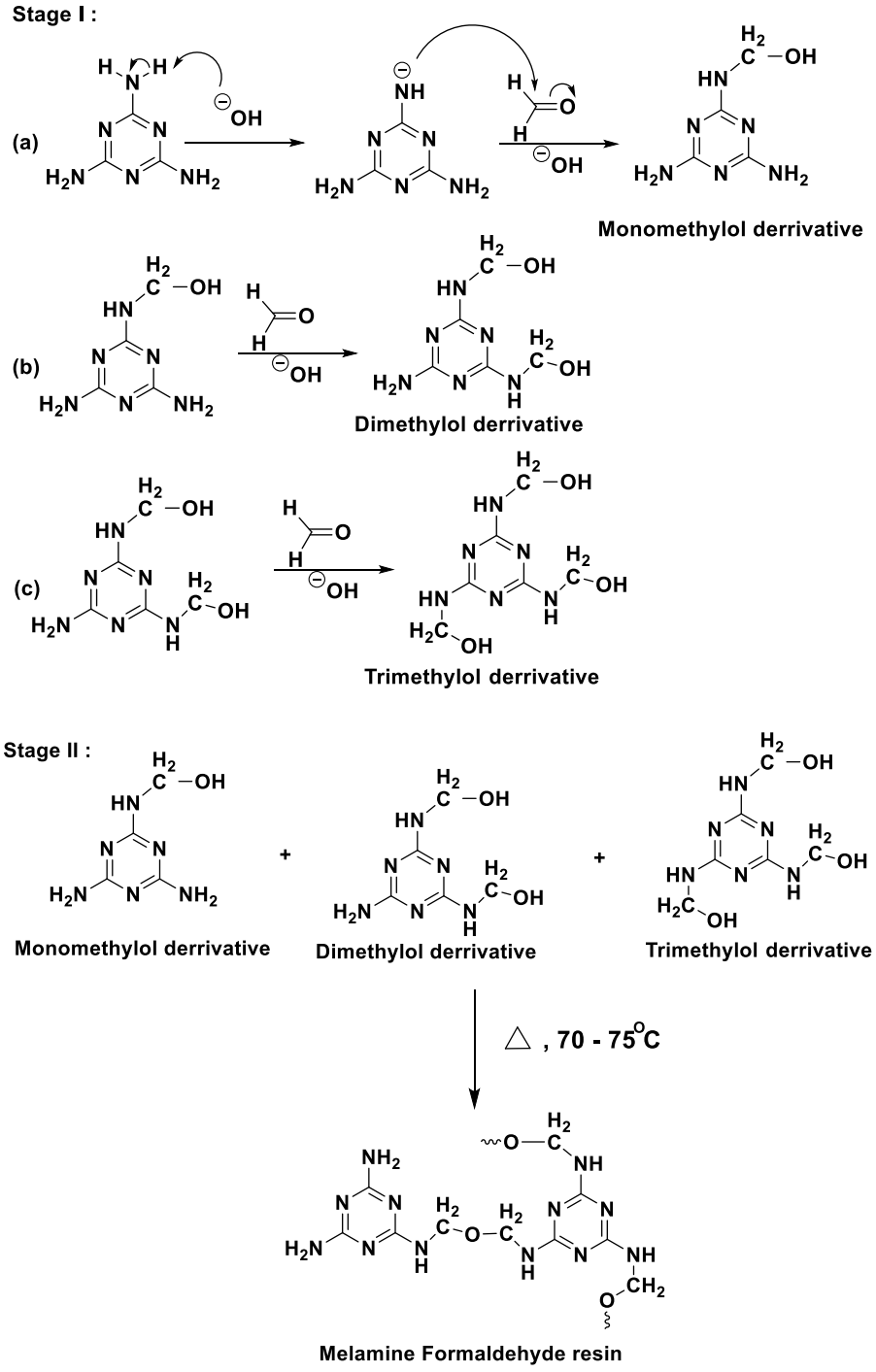

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Procedure:

1. The required ratio of formalin is first taken in a beaker an then neutralized using sodium hydroxide (NaOH) solution in presence of phenolphthalein indicator to remove excess acid present.

2. It is then transferred to a 3 neck flask & stirred till a temperature of 50^0C is attained.

3. Then add required amount of melamine & catalyst into the reaction flask & then whole mixture was continuously stirred and temp. at about 70-75^0C was maintained.

4. After addition of melamine there was slight increase in exotherm & therefore the mixture is continuously refluxed using water condenser.

5. The PH was maintained at 8-8.5 using sodium carbonate solution.

6. After attaining thermal equilibrium, the aliquot is refluxed for 30 minutes.

7. The reaction was stopped when a drop solution gives turbidity in water.

Calculation of weight of the reactants:

Assumption: Let us assume that X moles of phenol are required to prepare 250 gm. of MF resin.

Reaction:	$C_3H_6N_6$ +	3 HCHO	⟶	MF + H_2O	
Molecular Weight:	126.1	30		18	
Moles:	1	3		3	
Weight (gm.):	126.1	(30 *3)=90		(18*3)=54	
For X moles weight (gm.):	126.1**X**	**90X**		**250**	**54X**

Overall material balance: 126.1X+90X=250+54X

X = 1.5423 moles

Therefore, weight of phenol required = $\frac{126.1 \times X \times 100}{\%\ of\ purity}$ gm. = …….. gm.

Weight of formaldehyde required = 90 X = 90 * 1.5423 = 138.807 gm.

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Volume of formalin = 138.807/concentration of formalin ml. = …… ml.

Characterization:

(i) **Weight of the PP Petridis =** …… gm. (A)

(ii) **Weight of the PP Petridis + Product =** ……. gm. (B)

(iii) **Yield (%) =** $\frac{(B-A)\times 100}{250}$

(iv) **Solubility:** One gm. of the sample is taken in a beaker and 20 ml of the solvent is added to it.

Water	Acid	Alkali	Tetrahydrofuran	Acetone	Toluene

(v) Solid content: 1 gm. of the mixture is taken and dried in oven at 100 ˚C. The weight is measure after the complete drying of the sample.

Weight of the petridish = …… gm (A)

Weight of PP Petridish + Product (Before drying) = ……. gm.(B)

Weight of PP Petridish + Product (After drying) = ……. gm. (C)

Solid Content = $\frac{(C-A)}{(B-A)} \times 100$

(vi) **Viscosity:**

About 20ml of resin was taken in B ford cup viscometer keeping lower hole closed. It was then released & viscosity of resin was determined by using stopwatch. The procedure was repeated for 2-3 times till constant reading obtained.

(vii) **Formalin Content:**

Theory: Hydroxylamine hydrochloride reacts with free formaldehydes present in the sample and liberates HCl which is titrated against sodium hydroxide using bromophenol blue indicator.

Procedure:

(1) 0.1 (N) NaOH solution is prepared qualitatively in a 500 ml stoppered conical flask by dissolving 1.6 gm of NaOH in 400 ml of distilled water.

(2) 0.1 (N) Oxalic acid is prepared in a 100 ml. volumetric flask by accurately weighing 0.63 gm. in the said flask and make up the rest of volume with distilled water.

(3) Standardization of sodium hydroxide solution is performed by titrating it with 10 ml of oxalic acid solution (Primary Standard) using phenolphthalein indicator/Universal indicator.

(4) About 5 gm. of sample resin is weighed and dissolved in 10 ml of hydroxylamine hydrochloride in 100 ml conical flask.

(5) The mixture is then titrated under stirring condition against 0.1(N) sodium hydroxide using bromophenol blue indicator.

(6) Blank titration is carried out under identical condition using only 10 ml of hydroxylamine hydrochloride. end point is yellow to light violet.

[**Note**:

(iv) Sodium hydroxide solution should be taken in burette

(v) End point is detected by color change from colorless to pink (basic) for phenolphthalein indicator and yellow to light violet for bromophenol blue indicator.

(vi) After titration wash the burette thoroughly with water to remove sodium hydroxide from the burette. Then it should be rinsed several times with acetone before leave the room.]

Applications:

Assignment:

1. How is melamine prepared commercially?
2. What are the reactions that lead to the formation of melamine formaldehyde resins?
3. Mention properties and application of melamine formaldehyde.

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ACADEMIC YEAR: 2019-20 PART: II
COURSE: Polymer Synthesis-II COURSE CO-ORDINATOR: Ms. J.S.Suryawanshi

Experiment No. - 5

Aim: Synthesis of alkyd resin from glycerol & phthalic anhydride.

Apparatus:

3 Neck flask, mechanical stirrer, thermometer jacket, Dropping funnel with pressure equalizer, condenser, thermometer, water, heating mantle, funnel, dropper, measuring cylinder, rubber tube for water, glass rod , PP petridis, glass petridis (Large) etc.

Chemicals:

Coconut oil, Glycerol, Pthalic Anhydride, Litharge, Phenopthalein indicator, 0.5N KOH, Methanol etc.

Theory:

Theory: Alkyd resin are reaction products of polybasic acids & polyhydric alcohols that may or may not be modified with oils. It was used in surface coating industry. The resin was also inexpensive on cost performance basis & extremely versatile in performance. In manufacturing of alkyd two process used.

1. Monoglyceroid process.

2. Fatty acid Process.

Procedure:

1. Stoichiometric quantity of glyceroid & pthalic anhydride are weighed in the mole ratio of 1:1

2. Weighted amount of oil & glyceroid are taken in 3 neck flask.

3. The content was heated up to 250^0C to form monoglyceroid.

4. Initially oil was insoluble in methanol but the monoglyceroid was completely soluble in methanol.

5. As the formation of monoglyceroid is confirmed the heating was stopped & the temperature is brought up to the melting point of pthalic anhydride i.e. 121-125^{0}C.At this temperature add calculated amount of pthalic anhydride slowly & gradually.

6. Care should be taken to utilize each & every addition of pthalic anhydride.

7. If temp. goes above 130^{0}C sublimation of pthalic anhydride may takes place.

8. After complete addition of pthalic anhydride the assembly was connected in proper fashion.

9. The acid value of product was checked & heating was continued till the value reaches to 25-30 m.gm of KOH/gm of sample.

OR

Procedure:

1. Take 150 gm of linseed oil & heat in three neck flask in presence of nitrogen gas
2. It was heated to 180^0 C with constant stirring
3. A calculated amount of glycerol and litharge was added and temperature was increase to 240^0 C
4. The formation of mono glyceroid was tested in ethanol
5. The temperature was lowered to 180^{0}C and calculated amount of pthalic anhydride and gluceroid was added and heated to 240^{0}C till the acid value is reached below 10.
6. The alkyd was then cooled and thinned with spirit, viscosity was measured with 50%

Calculation: 1) Reaction

2)Purity of chemicals

3)Batch size & mole ratio

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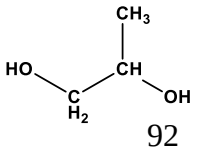
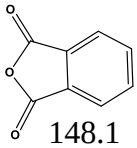
Calculation of weight of the reactants:

Assumption: Let us assume that X moles of propylene glycol are required to prepare 250 gm. of Alkyd resin.

Reaction:  +  → Alkyd + H_2O

Molecular Weight:	92	148.1		18
Moles:	1	1		1
Weight (gm.):	92	(148.1 *1)=148,1	(18*1)=18	
For X moles weight (gm.):	92**X**	**148.1X**	**250**	**18X**

Overall material balance: 92X+148.1X=250+18X

X = 1.1256 moles

Therefore, weight of Propylene Glycol required = $\frac{92 \times X \times 100}{\%\ of\ purity}$ gm. = …….. gm.

Weight of Phthaleic Anhydride required = 148.1 X = 148.1* 1.1256 = 166.701 gm.

Result:

1.Acid value of final product=

2.Weight of product=

3.Molecular weight=

4.Graph=Mol wt Vs Time

Application:

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Assignment:

1. What are alkyd resins? How are they prepared by the fatty acids process? Mention their important properties.
2. How are the alkyd resins prepaired by the monoglyceride process?

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ACADEMIC YEAR: 2019-20 PART: II
COURSE: Polymer Synthesis-II COURSE CO-ORDINATOR: Ms. J.S.Suryawanshi

Experiment No. - 6

Aim: Synthesis of Saturated Polyester.

Apparatus:

Resin Kettle, Dean & Stark apparatus, Thermometer, Stirrer, Heating mantle, Water condenser,Beaker, Measuring Cylinder, burette, pipette, conical flask etc.

Chemicals:

Adipic Acid, Ethylene glycol, KOH, Ethanol, toluene, phenopthalein indicator.

Theory: The product of Condensation polymerization between dibasic acid and diol are termed as polyester. The esterification can occur in five ways. They are Ester exchange reaction, Alcoholysis, Ring opening polymerization, Self condensation of ω-hydroxy acid and condensation of polyhydroxy compounds. The rate of reaction depends partly on whether the fundamental groups are primary or secondary. A homogeneous solution is essential for the carrying out this type of reaction. The reaction can be considered as polyesterification with stoichiometric amount of reactant.

An excess of glycol reacts with a hydroxyl terminated polymer if infinite size is called polyester glycol.

Acid value:

No. of m.gm of KOH equivalent to acidity present in 1gm of resin or

It is defined as no. of m.gm of KOH required to neutralize acid present per gm of sample**.**

Acid value procedure: one gm of sample was taken in conical flask & titrate it against 0.1N KOH using phenolphthalein indicator.

End point: Light pink to colorless.

Procedure:

1. Weight accurately both reactant (Adipic acid & ethylene glycol) & charge into resin kettle.

2. Heating was started with stirring the reaction mixture at about 20-25^0 C.

3. The temperature was raised slowly to 140^{0}C & the mixture was refluxed for 1-2 hrs so that dimmer was formed.

4. The reaction was carried out in presence of nitrogen gas at slow rate.

5. Then temperature was raised slowly to 200-220^{0}C.

6. Sample was analyzed for acid value after every hour.

7. Water to be removed with the help of dean-stark apparatus.

Calculation of weight of the reactants:

Assumption: Let us assume that X moles of propylene glycol are required to prepare 250 gm. of Alkyd resin.

Reaction:	**HOOC-$(CH_2)_4$-COOH** +	**HO-$(CH_2)_4$-OH**	⟶	Polyester +	H_2O
Molecular Weight:	146	62			18
Moles:	1	1			1
Weight (gm.):	146	(62 *1)=62			(18*1)=18
For X moles weight (gm.):	**146X**	**62X**		**250**	**18X**

Overall material balance: 146X+62X=250+18X

X = 1.316moles

Therefore, weight of adipic acid required = $\frac{146 \times X \times 100}{\%\ of\ purity}$ gm. = …….. gm.

Weight of ethylene glycol required = $\frac{62 \times X \times 100}{\%\ of\ purity}$ gm. = …….. gm.

= $\frac{62 \times X \times 100}{0.99}$ gm. = …….. gm.

Volume of ethylene glycol = $\frac{Weight\ of\ ethylene\ glycol}{Density\ of\ ethylene\ glycol}$

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$= \frac{\text{.....}}{1.11}$ gm./c.c.= …….. gm./c.c.

Result:

1.Acid value of final product=

2.Weight of product=

Application:

Assignment:

1. Write briefly on the general characteristics of polyester resins and the various fields of their applications.
2. What are the different classes in which polyester moulding compounds are generally available? How are the compounds prepared?
3. What are the effects of adding the following additives to an unsaturated polyester resin?

   Fillers b)Reinforcement c)Dyes & pigments d) Flame retardents

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ACADEMIC YEAR: 2019-20 PART: II
COURSE: Polymer Synthesis-II COURSE CO-ORDINATOR: Ms. J.S.Suryawanshi

Experiment No. - 7

Aim: Synthesis of Epoxy Resin.

Apparatus:

3 Neck flask, mechanical stirrer, thermometer jacket, Dropping funnel with pressure equalizer, condenser, thermometer, water, heating mantle, funnel, dropper, measuring cylinder, rubber tube for water, glass rod , PP petridis, glass petridis (Large) etc.

Chemicals:

BisPhenolA and Epichlorohydrin, sodium hydroxide, toluene.

Theory:

Procedure:

1. BisPhenol-A & epichlorohydrin (1:4 moles) was heated to about 60^0C while stirring.

2. Solid NaOH (2mole per mole of bisphenol A) was added slowly at such a rate that the reaction mixture remains neutral.

3. The reaction was exothermic & cooled to 60^0C temp.

4. Excess of epichlorohydrin was then remove by distillation under reduce pressure.

5. This epoxy resin was mixed with sodium chloride then filtered off, toluene was added to the mixture in order to facilitate filtration.

6. The toluene was removed & then the resin was heated at 150^0C to remove trace of volatile matter.

7. Finally the resin was collected on filter paper.

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Procedure:

1. 1mole of bisphenol A was dissolved in 4 moles of epichlorohydrin & the mixture was heated to 105-110^0 C under an atmosphere of nitrogen.

2. Prepare 2 mole of NaOH.

3. Add drop wise NaOH solution to the reaction mixture. The temp. of the mixture is maintained between 100-115^{0}C.The reaction was exothermic hence external heating may not be required.

4. The reaction was stirred for 14-15 hr.

5. After completion of reaction remove excess of epichlorohydrin by distillation & water was removed by vacuum application at 110^{0}C for 30 min.

6. Wash the product with toluene.

7. Separates the product by filtration & distilled of toluene from resin.

Calculation:

1) Reaction

2)Purity of chemicals

3)Batch size & mole ratio

X Bisphenol A + 4X Epichlorohydrin ----------→ 250+XH_2O

228.29X+370X----------→250+18X

598.29X-18X----------→250

580X=250

Therefore X=0.43

Therefore weight of bisphenol A required

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228.29X 228.29*0.43

---------- = ---------- = 99.156 gm

% of purity 0.99

therefore weight of epichlorohydrin required

92.52*4X 92.52*4*0.43

---------- = ---------- = 160.74 gm

% of purity 0.99

Result:

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ACADEMIC YEAR: 2019-20 PART: II
COURSE: Polymer Synthesis-II COURSE CO-ORDINATOR: Ms. J.S.Suryawanshi

Experiment No.-8

Aim: To determine the epoxy equivalent weight by hydrogenation method.

Apparatus: Beaker,Burette,Conical flask

Chemicals:

1. Hydro chlorination reagent (25 ml of 0.2N HCL is added to one liter of pure dioxin or MEK).

2.0.1 N alcoholic NaOH.

3. Phenopthalin/Cresol red/Bromophenol blue indicator.

Defination:

Epoxy value is defined as the no. of epoxy groups per 100 parts of sample & epoxy equivalent is defined as the weight corresponding to epoxy value.

Procedure:

1. Weigh 1 to 2 gm of sample.

2. Add to it 25 ml of hydro chlorination reagent.

3. Shake it vigorously & allow to stand for 15min.

4. Add few drops of indicator & titrate excess of acid with 0.1N NaOH.

5. Though acid content is negligible determine the acidity or basicity of the sample by titrating with standard alcoholic base or acid. Take blank reading.

Calculation:

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$$\text{Epoxy Eqvivalent} = \frac{W*1000}{\text{Blank - Sample Volume}} * \text{Normality of NaOH}$$

$$\text{Epoxy Value} = \frac{100}{\text{Epoxy Eqvivalent}}$$

Result: