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SYNTHESIS AND CHARACTERIZATION OF CROSSLINKED POLYMER BASED ON CYCLOPENTANONE CONTAINING ZINC METAL

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ABSTRACT

Two novel crosslinked polymers are synthesized using the crosslinker 2,6 – bis (4- methacryloyloxy benzylidene) cyclopentanone (BMACP). The crosslinker is prepared using the reaction between the cyclopentanone based arylidine compounds with the methacryloyl chloride. The two crosslinked polymers were prepared using commercially available monomers Styrene (s) and N-vinyl-2-pyrrolidone (NVP). The crosslinking polymerization is prepared in the presence of zinc acetate to make the novel copolymer as metal incorporated copolymers. The product indeed formed. The formed BMACP and crosslinked polymers were well characterized using the available techniques like FTIR, NMR and TGA analysis. The formed crosslinked polymers can be highly useful for the organic compound synthesis as a heterogeneous catalyst.

KEYWORDS*: Cyclopentanone, arylidine, styrene, copolymer.*

1.INTRODUCTION

Polymeric proton-conducting electrolytes possess intrinsic proton conductivity from the functional group in the polymer chains, whereas the inorganic/polymer proton-conducting electrolyte operates by mixing of inorganic proton conductors with a polymeric matrix to form gels or composites. Most proton-conducting materials have been extensively studied for fuel cell applications. However, due to the higher operating temperature of fuel cells compared to supercapacitors, the development of low to room temperature proton conducting polymer electrolytes has been limited. In order to design and optimize suitable proton-conductors as electrolytes for solid supercapacitors,
it is essential to understand the proton migration mechanisms below or at room temperature. Inorganic/polymer proton-conducting electrolytes can be supplemented separated into two subgroups: (a) salt-in-polymer and (b) polymer-in-salt. Salt-in-polymer electrolytes are prepared by dispersing acids, bases, or salts in a polymer such as PEO (1), poly(acrylonitrile) (PAN), or poly(methylmethacrylate) (PMMA) (2). Most salt-in-polymer electrolytes are aqueous based and form acid/polymer blends or acidic hydrogels (i.e. aqueous gels). In contrast, polymer-in-salt electrolytes are prepared by using only a small amount of polymer material as a matrix to hold the solid proton conductors together during film forming. Polymers used in such systems include PEO, PVA (3), and poly(vinylpyrrolidone) (PVP) (4). H_2SO_4 and H_3PO_4 are often chosen as proton conductors due to their self-ionization and self-dehydration reactions (5) at pure states. Solid polymer electrolyte has good stability and amorphous in nature. In this work copolymer is synthesized in the presence of conducting moiety zinc acetate and characterized.

2. Experimental section

2.1. Purification of solvents and reagents

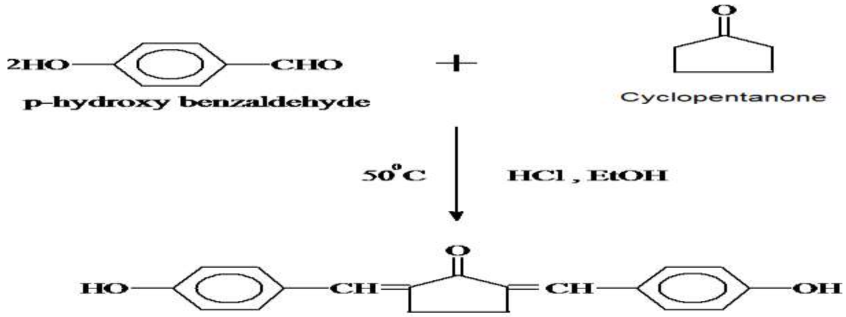
All the solvents such as chloroform, benzene, tetrahydrofuran, dimethyl sulphoxide, dimethyl formamide, methanol, ethanol, MEK, Triethyl amine, Zinc acetate and acetone were purchased from Aldrich chemicals and used as such. Initiator, benzoyl peroxide (LR) was recrystallised using 1:1 v/v mixture of chloroform and methanol. Extra pure Styrene was obtained by vacuum distillating the commercial sample to remove the inhibitor. N-vinyl-2-pyrrolidone was freed from inhibitor before using for copolymerisation by vacuum distillation.

2.2. Characterisation.

The solubility of the monomer and the polymers were tested in several protic and
aprotic solvents at room temperature. 0.02g of the sample was taken in 10mL of the solvent and kept overnight. Their solubility was noted. The IR spectra of the monomer, homopolymer and copolymers is done by a KBr pellet method using Bruker FT-IR Spectrometer. ^{1}H NMR Spectra of samples were run on a Bruker 500MHz Spectophotometer at room temperature using $CDCl_3$ and DMSO as solvents and TMS as internal reference. Thermal analysis of prepared film was found using DuPont 951 thermo gravimetric analyzer. The sample is heated from 30 to 800 °C at the heating rate of 10 °C/min in an inert atmosphere with a gas flow rate of 100 mL/ min.

2.3 Preparation of 2,6 –bis (4- hydroxy benzylidene) cyclopentanone (BHBCP) (Scheme 1).

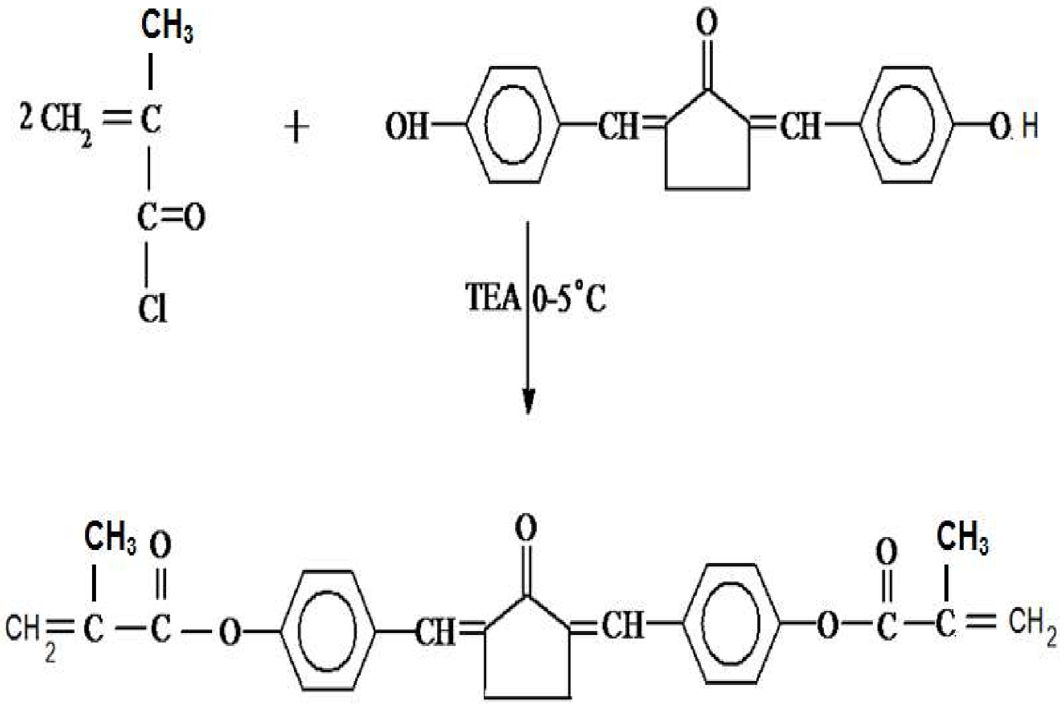
24.4 gm (0.2 mole) of p- hydroxy benzaldehyde and 11.44 ml (0.1 mole) of cyclopentanone were placed in a 500 mL round bottom flask contain 100 ml of ethanol. Then the catalyst (HCl (g)) which is used for the reaction has been produced by the reaction of conc. H_2SO_4 and powdered NaCl, which then passed into the reaction mixture at room temperature. After 2h the contents of the flask were filtered. The military green precipitated is kept for drying in vaccum oven. Yield: 92.5%; m.p: >190 °C.



Scheme 1: Synthesis of 2,6 -bis (4- hydroxy benzylidene) cyclopentanone (BHBCP)

2.4 Preparation of 2,6 – bis (4- methacryloyloxy benzylidene) cyclopentanone (BMACP) (Scheme 2).

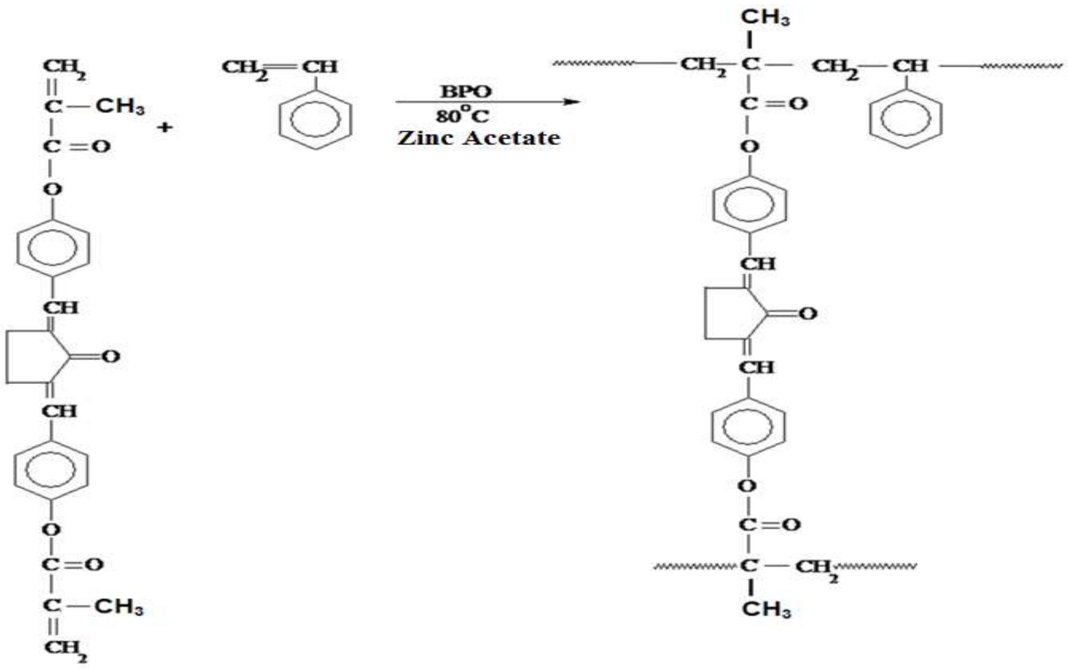
In a three-necked bottom flask fitted with a mechanical stirrer, 0.017moles (5.27g) of BHBCP, 0.04moles (5.6 ml) of triethyl amine, and 250ml of EMK were placed. 0.036mol (3.7ml) methacryloyl chloride dissolved in 25ml EMK taken in a pressure equaliser was added in drips at 0-5 °C for roughly half an hour after thorough mixing. The round bottom flask was kept in an ice bath during the addition of the reagents to maintain the appropriate temperature. After the addition, the stirring was continued at room temperature for another three hours. The organic layer was then dried with anhydrous sodium sulfate after the reaction mixture was filtered and the filtrate produced was washed with 60 mL of distilled water in parts. By evaporating the solvent, the product was obtained. Yield: 78%; m.p: 155 °C.



Scheme 2: Synthesis of 2,6 - bis (4- methacryloyloxy benzylidene) cyclopentanone (BMACP)

2.4. Copolymerisation of BMACP, Zinc acetate and Styrene (Scheme 3).

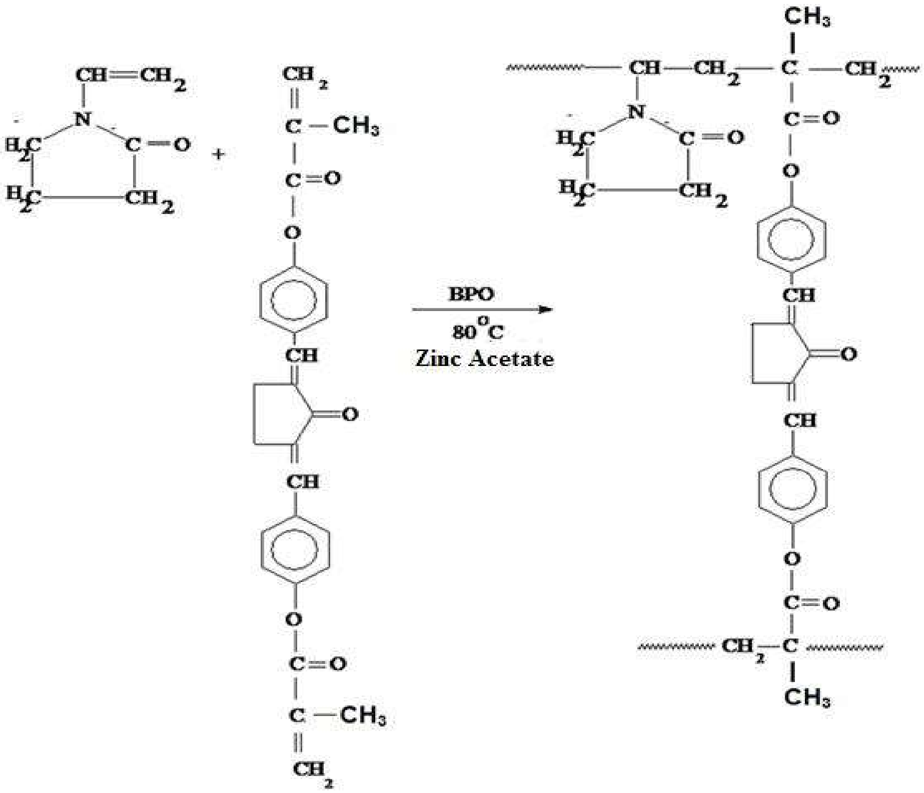
Suspension polymerization was used to create the copolymer. In a polymerization tube containing EMK as a solvent and BPO (2 percent w/w) as an initiator, an equimolar ratio of BMACP, Zinc acetate, and styrene were used. By sending nitrogen gas through the polymerization tube's inlet, the reaction medium was rendered inert. The polymerization took place at 70±1°C. The solution was precipitated into methanol, and the resulting precipitate was filtered through a sintered crucible, washed in methanol, and weighed.



Scheme 3: Synthesis of crosslinked polymer based on styrene

2.4. Copolymerisation of BMACP, Zinc acetate and N-Vinyl Pyrrolidone (NVP) (Scheme 4).

In a polymerization tube containing EMK as a solvent and BPO (2 percent w/w) as an initiator, an equimolar mixture of BMACP, Zinc acetate, and NVP was added. By sending nitrogen gas through the polymerization tube's inlet, the reaction medium was rendered inert. The polymerization took place at 70±1°C. After that, the solution was precipitated into methanol, and the resulting precipitate was filtered and washed in methanol.



Scheme 4: Synthesis of crosslinked polymer based on N-Vinyl Pyrrolidone

RESULT AND DISCUSSIONS

3.1.Synthesis of 2,6 –bis (4- hydroxy benzylidene) cyclopentanone (BHBCP).

The compound BHBCP was synthesized by reacting p-hydroxy benzaldehyde and cyclopentanone at 50 °C in the presence of HCl gas using ethanol as a solvent. The formation of the product is confirmed by the IR and NMR techniques. IR spectrum of BHBCP was shown in the Figure 1. The peak at 3258 is due to the aromatic OH. The peak appears at 3033 and 2968 related to the aromatic and aliphatic CH stretching frequency respectively. The appearance of peak at1679 is due the carbonyl C=O stretching and the vinylic peak appears at1604 cm^{-1}. The ^1H NMR spectrum of BHBCP was shown in the Figure 2. Characteristic chemical shifts of different groups present in the spectrum were listed as 10 (b, phenolic OH), 7.3 (s, vinyl type CH), 7.0 (s, vinyl type CH), 7.5-8.3(m, aromatic protons) and 1.9-2.5 (m, cyclopentanone ring protons).

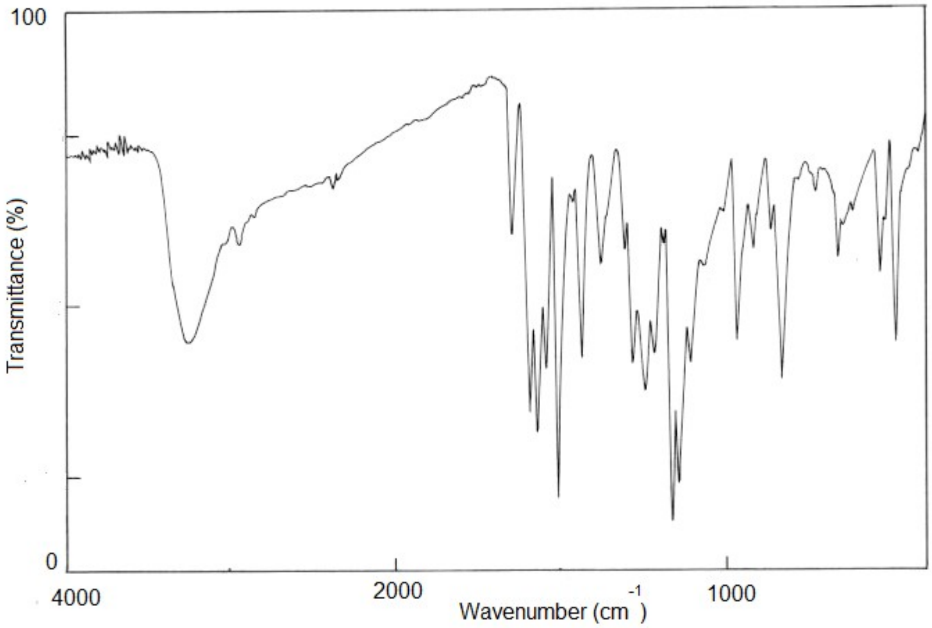


Figure 1: FTIR spectrum of BHBCP

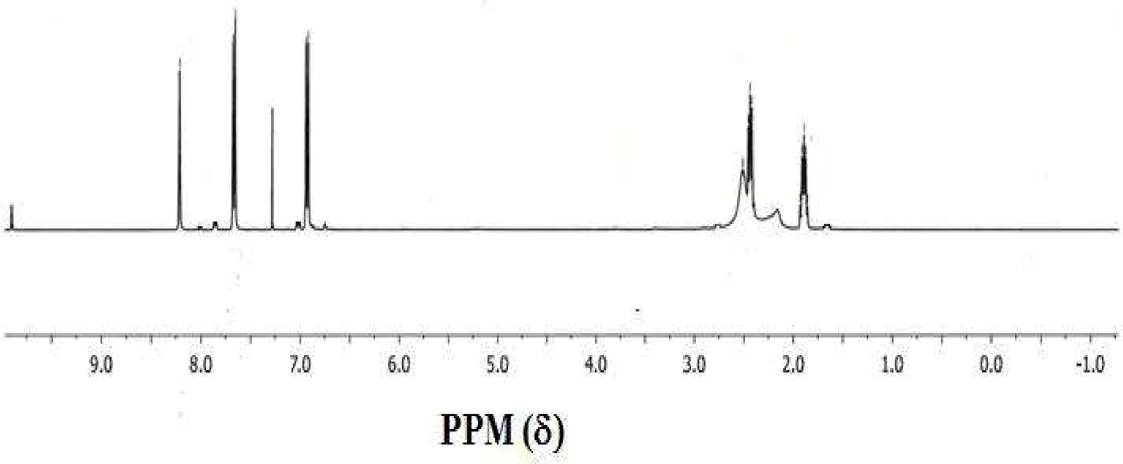


Figure 2: ^1H NMR spectrum of BHBCP

3.2 Synthesis of 2,6 – bis (4- methacryloyloxy benzylidene) cyclopentanone (BMACP).

The crosslinker was synthesized by reacting 2,6 –bis (4- hydroxy benzylidene) cyclopentanone with methacryloyl chloride in the presence of triethyl amine using EMK as a solvent. The formation of the product is confirmed by the IR and NMR techniques. IR spectrum of BMACP was shown in the Figure 3. The absence of peak around 3250 confirms that the OH group is completely reacted with methacryloyl chloride. The peak appears at 3058 and 2934 related to the aromatic and aliphatic CH stretching frequency respectively. The presence peak at 1726 is due to the ester carbonyl group. The appearance of peak at 1666 is due the carbonyl C=O stretching and the vinylic peak appears at1603 cm^{-1}. The presence of O=C-O is confirmed by the appearance of a peak around 1201-1137 cm^{-1}. The ^{1}H NMR spectrum of BMACP was shown in the Figure 4. Characteristic chemical shifts present in the spectrum was, 7.0-8 (m, aromatic protons), 6.5 (m, polymerizable vinyl protons), 1.1 (CH_3 proton) and 1.5-2.4 (m, cyclopentanone ring protons).

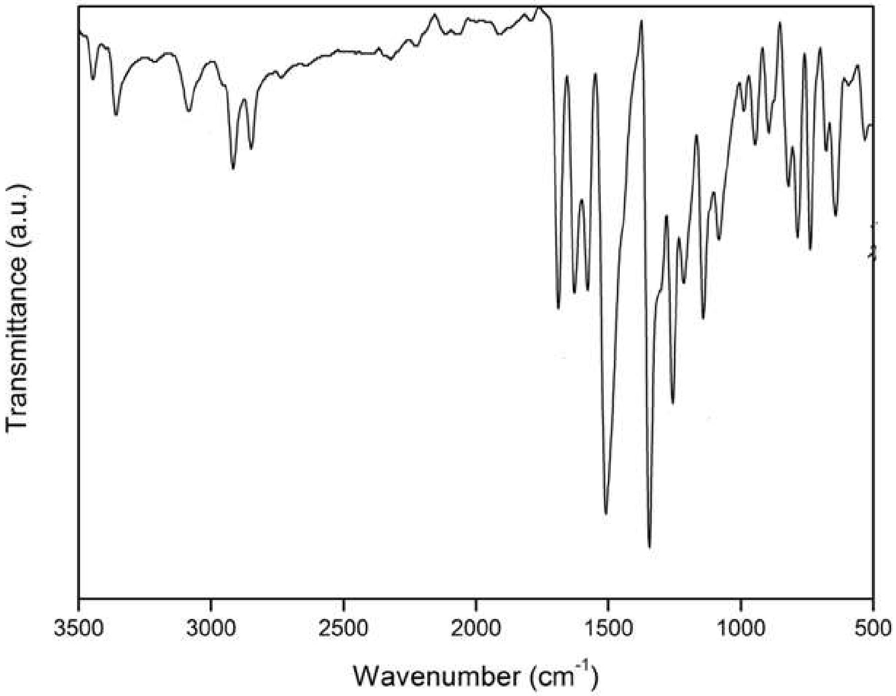


Figure 3: IR spectrum of BMACP

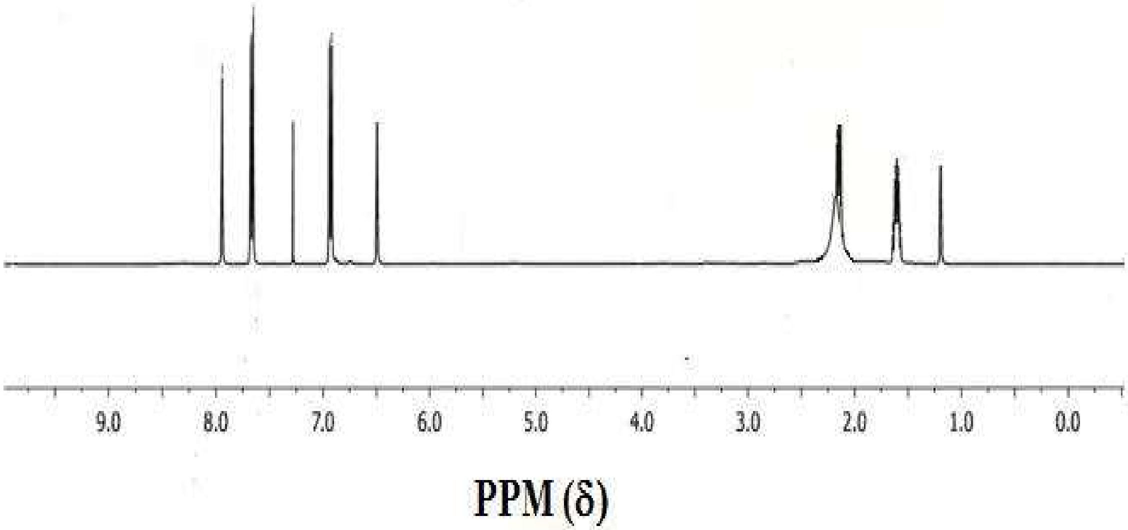


Figure 4: ^{1}H NMR spectrum of BMACP

3.3.Copolymerisation of Styrene, zinc acetate with the addition of 2,6 – bis (4- methacryloyloxy benzylidene) cyclopentanone [BMACP].

Comopolymers of styrene and zinc acetate with the addition of 2,6 – bis (4- methacryloyloxy benzylidene) cyclopentanone were synthesized in an nitrogen atmosphere using EMK as a solvent. The temperature maintained is 80±1 °C for about 10-12 hrs. after the reaction is complete, the product is processed and is dried in vacuum at 40 °C. The formation of the product is confirmed by the IR and NMR techniques. IR spectrum of poly(S-co-BMACP) containing zinc acetate was shown in the Figure 5. The peak appears at 3033 and 2968 related to the aromatic and aliphatic CH stretching frequency respectively. The presence peak at 1722 is due to the ester carbonyl group. The appearance of peak at 1665 is due the carbonyl C=O stretching and the vinylic peak appears at1595 cm^{-1}. The presence of O=C-O is confirmed by the appearance of a peak around 1245-

1157 cm^{-1}. The ^1H NMR spectrum of poly(S-co-BMACP) was shown in the Figure 6. Chemical shifts corresponding to the characteristic protons present in the spectrum were listed. 8.3-7.0 (aromatic protons, m), 2.0-2.3 (polymer chain aliphatic proton, m), and 1.0 (CH_3, aliphatic protons,).

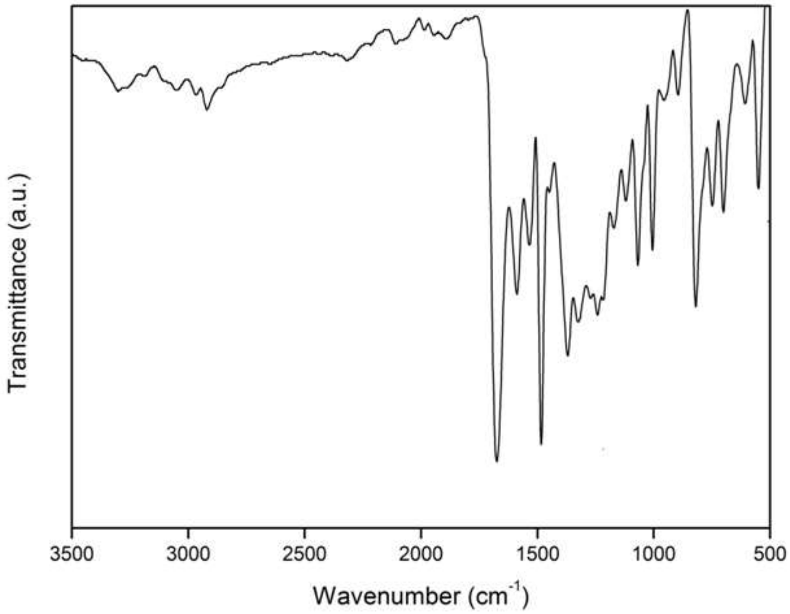


Figure 5: IR spectrum of poly(S-co-BMACP) contain zinc

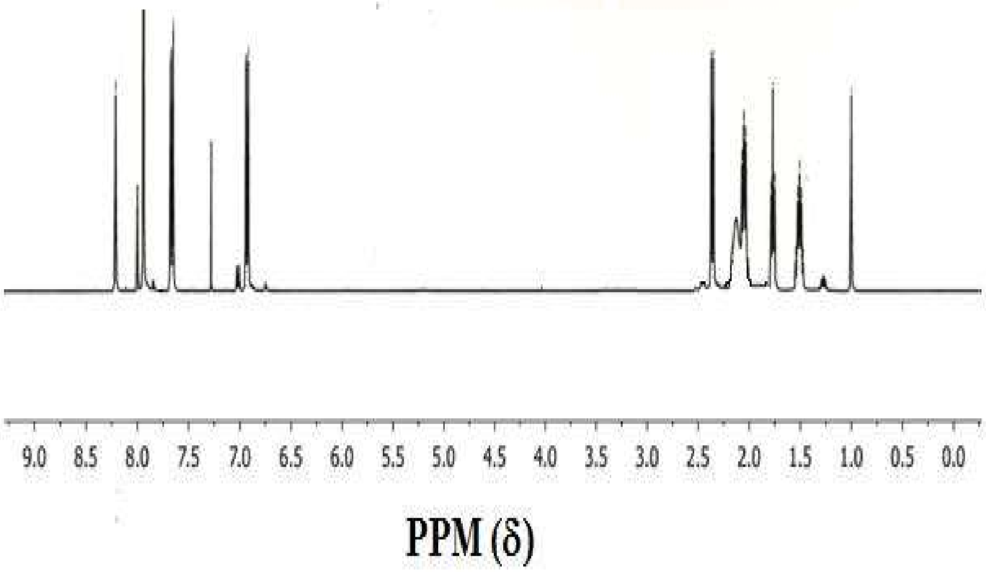


Figure 6: ^1H NMR spectrum of poly(S-co-BMACP) contain zinc

3.4 Comopolymerisation of N-Vinyl Pyrrolidone (NVP), zinc acetate with the addition of 2,6 – bis (4- acryloyloxy benzylidene) cyclopentanone[BMACP].

Comopolymers of N-Vinyl Pyrrolidone, zinc acetate with the addition of 2,6 – bis (4- methacryloyloxy benzylidene) cyclopentanone were synthesized in a nitrogen atmosphere using EMK as a solvent. The temperature maintained is 80±1 °C for about 10-12 hrs. After the reaction is complete, the product is processed and is dried in vacuum at 40 °C. The formation of the product is confirmed by the IR and NMR techniques. IR spectrum of poly(NVP-co-BMACP) containing zinc acetate was shown in the Figure 7. The peak appears at 3048 and 2975 related to the aromatic and aliphatic CH stretching frequency respectively. The presence peak at 1719 is due to the ester carbonyl group. The appearance of peak at 1653 is due the carbonyl C=O stretching and the vinylic peak appears at1600 cm^{-1}. The presence of O=C-O is confirmed by the appearance of a peak around 1210-1152 cm^{-1}. The ^1H NMR spectrum of poly(S-co-BMACP) was shown in the Figure 8. Chemical shifts present in the spectrum was listed as, 7.0-8.3 (m, aromatic), 3.6 (NVP proton), 1.5-2.2 (Polymer chain proton), and 1.0 (CH_3 Proton).

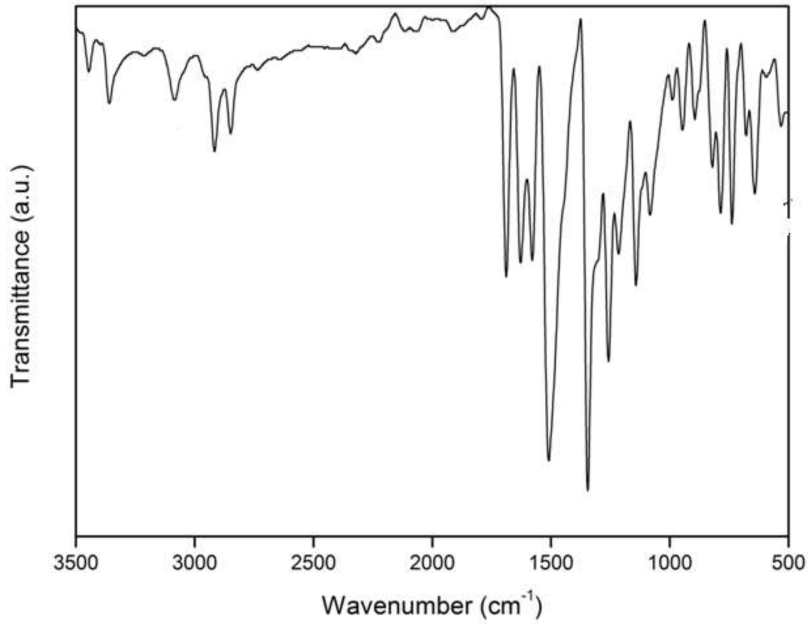


Figure 7: IR spectrum of poly(NVP-co-BMACP) contain zinc

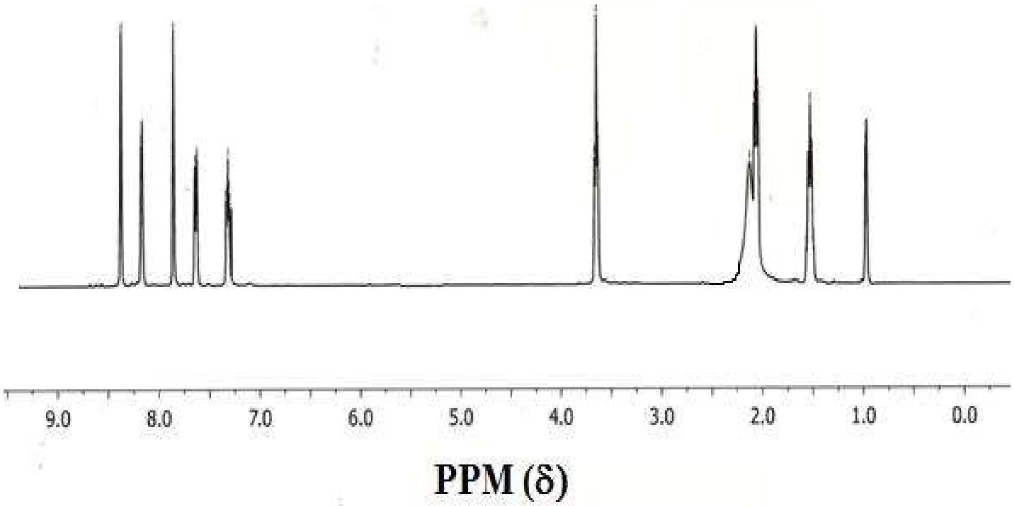


Figure 8: ^{1}H NMR spectrum of poly(NVP-co-BMACP) contain zinc

3.5. Solubility of the polymers

The solubility data of the polymers were presented in the Table 1. The table confirms that the polymers are soluble in the highly polar solvents like DMSO and DMF. Polymers are insoluble in the water, methanol and ethanol. Polymers also insoluble in the nonpolar solvent like hexane and cyclohexane.

Table 4.1. Solubility data of homo and copolymers at 30 °C

Name of compound	Water	MeOH	EtOH	CCl_4	$CHCl_3$	DMSO	DMF	Acetone	THF	Hexane	Benzene
BMACP	-	+	+	±	+	+	+	+	+	-	±
P(Styrene) with BMACP	-	-	-	-	-	Ξ	Ξ	-	Ξ	-	-
P(NVP) with BMACP	-	-	-	-	-	Ξ	Ξ	-	Ξ	-	-

Where,
- =Insoluble; ±=Sparingly soluble; +=Soluble; Ξ=Swelling of the sample

3.6. Thermogravimetric analysis (TGA)

TGA analysis of poly(S-co-BMACP) and poly(NVP-co-BMACP) were presented in the Figure 9 and 10 respectively. The percentage decomposition temperature of the studied polymers was shown in the Table 2. Both the polymers showed two stage decomposition temperature. The initial decomposition temperature of the n-vinyl pyrrolidone based polymer is lower than the styrene based polymer. In both the case the final residual value is not zero confirms that the polymers were completely decomposed at elevated temperature and the residual percentage is due to the metal which is incorporated in the copolymer.

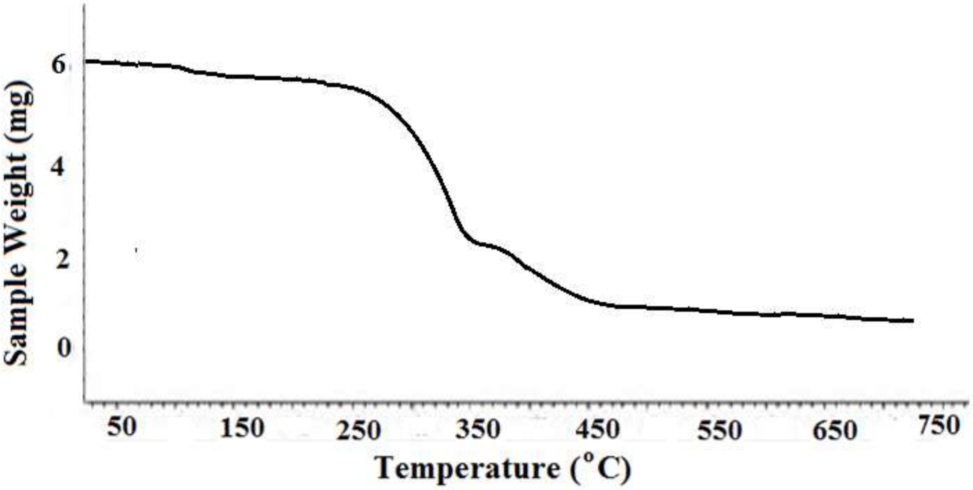


Figure 9: TGA spectrum of poly(S-co-BMACP) contain zinc

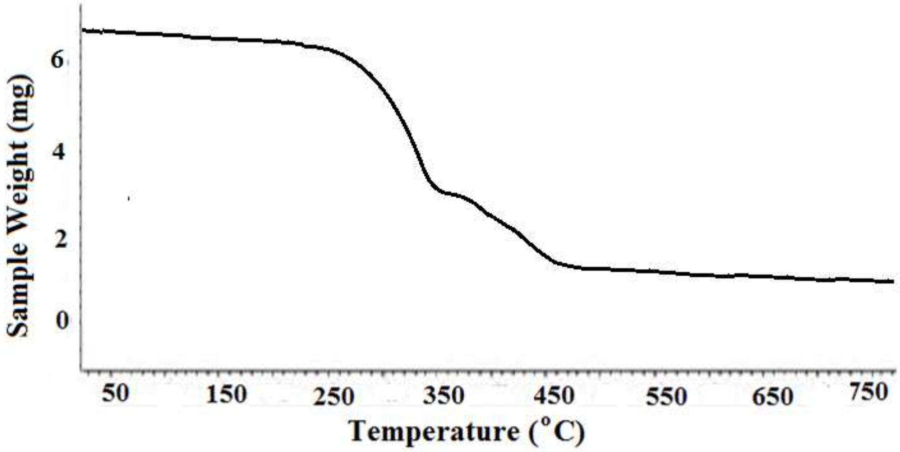


Figure 10: TGA spectrum of poly(NVP-co-BMACP) contain zinc

Table 2.Thermal decomposition data of poly(S-co-BMACP) and poly(NVP-co-BMACP)

Name of the polymer	IDT*, (°C)	% Weight loss at different temperatures (°C)								
		10%	20%	30%	40%	50%	60%	70%	80%	90%
poly(S-co-BMACP)	252	268	275	303	324	346	395	399	421	435
poly(NVP-co-BMACP)	249	268	289	302	326	340	366	402	428	445

* = Initial Decomposition Tempertaure

4. CONCLUSION

Chalcone type compound BHBCP was prepared from cyclopentanone and para hydroxyl benzaldehyde. Crosslinker BMACP is synthesized using the BHBCP and methacryloyl chloride at a low temperature. The crosslinker is charecterised by IR and NMR technique and found that the formed product is desired one. A series of crosslinked polymers along with zinc acetate, poly(BMACP-co-S) and poly(BMACP-co-NVP) were prepared by solution polymerization technique. The synthesized polymers were characterized by IR, NMR and TGA techniques. The IR and NMR spectra confirm the formation of the desired product. The TGA spectrum showed around 10% residue which can be due to the metal present in the copolymer. The final product can be useful as a catalyst for the organic reactions and that could be useful for the industrial applications.

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