Modification of vinyl chloride copolymer to Schiff base

Enaam Fadil Mousa
Department of Chemistry
College of Science for Women University of Baghdad

Abstract :

Several new Schiff base derivative were prepared by condensing various aldehydes and ketones (aliphatic and aromatic) with vinyl chloride copolymer hydrazine in presence of acid catalyst under reflux condition . All the compounds have been characterized on the basis of their softening points ,Viscosity and FT-IR spectral data .

Introduction

A heteropolymer or copolymer is a polymer derived from two (or more) monomeric species, as opposed to a homopolymer were only one monomer is used [(1)] , from vinyl chloride and vinyl acetate copolymer derived by the polymers . This research include modifies vinyl chloride copolymer to Schiff base . Schiff base (or azomethine) names after Hugo Schiff [(2)], who synthesized such compounds . These are the compounds containing a carbon – nitrogen double bond with the nitrogen atom connected to an aryl group or an alkyl group but not hydrogen [(3,4)]. The chemistry of the carbon – nitrogen double bond plays a vital role in the progresses of chemistry science [(5)] . Schiff bases can be synthesized from an aromatic amine and a carbonyl compound by nucleophilic addition forming a hemiaminal , followed by a dehydration to generate an imine[(6,7)].

Schiff bases are the important compound owing to their wide range of biological activities and industrial application. they have been found to posses the pharmacological activities such as antimalarial [(8)] , anticancer [(9)] , antibacterial [(10)] , antifungal [(11)] , antitubercular [(12)] , antiinflammetery , antimicrobial [(13)] , antiviral [(14)] and as herbicides [(15)] . On the industrial scale , they have a wide range of applications such as dyes and pigments [(16)] . Schiff bases are used as substrates in the preparation of a number of industrial and biologically active compounds via closure, cycloaddition and replacement reactions [(17)]. In view of these above biological importance of Schiff bases .I plane to synthesis of some novel vinyl chloride copolymer derivative analogs to Schiff bases by Schiff reaction .

Experimental

Material

All chemical compound were obtained from Fluka or Aldrich .

Preparation of Vinyl Chloride Copolymer Hydrazine (1)

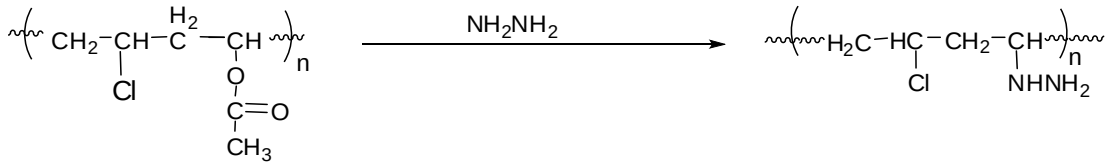
By dissolving (1gm) of vinyl chloride copolymer in (25ml) of THF , then taked (10ml) of the prepared solution and added (5ml) of hydrazine drop by drop with stirring appeared oily dropsof the yield (1) . By separation funnel it was separated and leaved until the all solvent (THF) evaporated . The yield was white color polymer

General procedure for the synthesis of Schiff bases of vinyl chloride copolymer hydrazine (2-10)

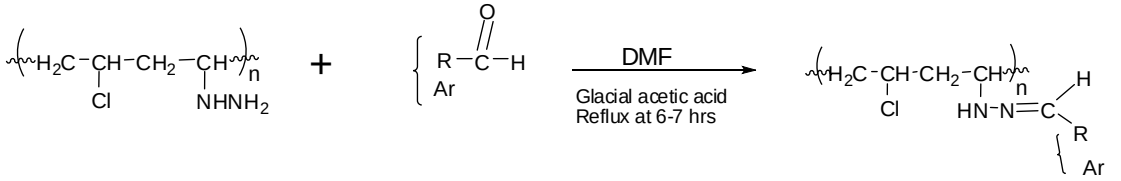
The Schiff base was prepared by reaction of 0.5gm of vinyl chloride copolymer hydrazine (1) or aliphatic and aromatic aldehydes or ketones . The reactant (1) was dissolved in 20ml of DMF , then added 1gm or 1ml of the aldehyde or ketone to the solution of the substance (1) , then mixed together and followed by addition of four drops of glacial acetic acid [18].The solution was refluxed for 7hrs , then cools to room temperature and poured into big dish and leaves for 24hrs after 24hrs the solid product was collected through the decantation and then dried using drying oven at 50°C . The product was redissolved in DMF and precipitated in water except compounds 2 and 10 were not soluble in DMF and another solvent then dried to give a product (a copolymer), Scheme 1, Scheme 2, Scheme 3 and Scheme 4, physical properties of the products are listed on table (1).

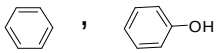
Scheme : 1

Synthesis of vinyl chloride copolymer hydrazine (1)



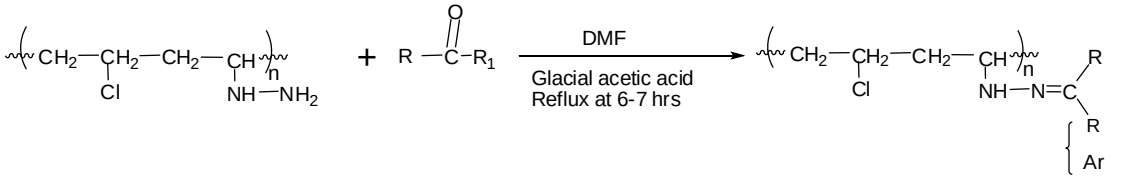
Synthesis of Schiff bases (2-5) **Scheme :2**

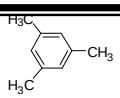


R = H , CH_3 ,Ar =  (2-5)

Scheme : 3

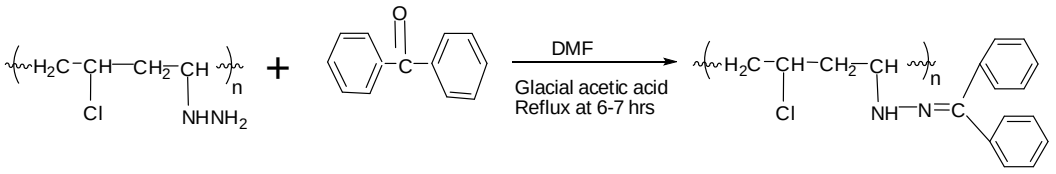
Synthesis of Schiff bases (6-9)



$R_1 = CH_3, C_2H_5$ $R = CH_3$ Ar =  , 

(6-9)

Scheme : 4
Synthesis of Schiff bases (10)



(10)

Table (1) : Physical properties of the prepared compounds .

Comp. No.	Molecular Formula	M.Wt	Conversion %	Softening Point°C	η dl/g	Color
1	$C_4H_9N_2Cl$	120.5	72	198	0.49	White
2	$C_5H_9N_2$ Cl	132.5	70	240	---	Brown
3	$C_6H_{11}N_2$ Cl	146.5	80	168	1.3	Yellow
4	$C_{11}H_{13}N_2$ Cl	208.5	73	138	0.29	Orange
5	$C_{11}H_{13}N_2$ ClO	224.5	72	184	0.42	Yellow
6	$C_{11}H_{13}N_2$ Cl	160.5	73	152	0.61	Yellow
7	$C_8H_{15}N_2$ Cl	174.5	76	122	0.74	Yellow
8	$C_{12}H_{14}N_2$ Cl_2	257	71	154	0.42	Brown
9	$C_{15}H_{21}N_2$ Cl	264.5	71	162	0.35	Brown
10	$C_{17}H_{17}N_2$	249	70	260	---	Dark brown

Results and Discussion

The synthesis of Schiff bases of vinyl chloride copolymer hydrazine (2-10) involved first, the reaction of vinyl chloride copolymer with hydrazine hydrate to product compound (1) second , the compound (1) was treated with various aldehydes or ketones (aromatic or aliphatic) to yield the compounds (2-10) Schiff bases .

The structure of compounds (1-10) were confirmed by physical properties , which are listed on table (1) and FT-IR spectral data .

From the results of viscosity of the copolymers (3, 6 ,and 7) , illustrated that copolymers 3,6 ,and 7 were have high molecular weights , while the copolymers (2 and 10) were have not results of the viscosity , because of there is no solvent solves in it .

FT-IR spectrum for compound (1) showing the absorption at (3414 cm^{-1}) (N-H str of –NH) , (3282 – 3228 cm^{-1}) (N-H str of $–NH_2$) ,1130 cm^{-1} (C-N str), 1454 cm^{-1} (N-N bending) , which confirming the reaction of vinyl chloride copolymer with hydrazine hydrate, which are listed on table(2) .

The FT-IR spectra of the compounds (2-10) (Schiff bases) showed absorption band at (1674 – 1616) cm^{-1} indicated the stretching vibration of (-C=N-) Schiff base and disappearance the absorption at (3282, 3228) cm^{-1}(N-H str of $–NH_2$) , which confirming the condensation of reactants. The other peaks of FT-IR spectra prove the structure of Schiff base derivatives , which are listed on table (2) .

Table (2) : FT-IR absorption spectra data (cm^{-1}) of the prepared compounds .

Comp.No.	ν NH ν NH_2	νC = N	ν C-N C-N bending	N-N bending	ν C=C	Other bands
1	3414 3282,3228		1323 1130	1454		νC-H alph. 2993-2978
2	3414	1639, 1674	1330 1095	1435		νC-H alph. 2912-2854
3	3437	1635, 1670	1327 1111	1435		νC-H alph. 2970-2870
4	3437	1639, 1658	1330 1095	1435	1492	νC-H aromatic,3062 νC-Halph.2935- 2862
5	3452	1666	1327 1095	1431	1496 ,1546	νC-H aromatic,3062 νC-H alph. 2912-2866
6	3460	1639	1327 1103	1431		νC-H alph. 2974-2843
7	3417	1616	1330 1103	1435		νC-H alph. 2962-2858
8	3417	1600, 1658	1315 1111	1442	1496	νC-H aromatic,3059 νC-H alph 2974- 2870
9	3417	1627, 1658	1327 1103	1431	1462, 1527	νC-H aromatic,3065 νC-H alph. 2974-2908
10	3406	1654	1319 1122	1446	1597, 1577	νC-H aromatic,3055 νC-H alph. 2954-2904

References

1. Odian, G . Principles of Polymerization . Wiley – Interscience, 6 , 464 , 2004.
2. Schiff H , Justus Liebigs Ann Chem., 131 , 118 – 119 , 1864 .
3. J . J . Vora , S . B . Vasava , K . C . Parmar , S . K . Chauhan and S . S .Sharma , E – J . Chem . 6(4) , 1205 – 1210 , 2009 .
4. IUPAC Compendium of chemical terminology , 67 , 1364 , 1995 .
5. S . Patai , The chemistry of the carbon – nitrogen double bond , John Wiley and Sons Ltd ., London , 1970 .
6. A . J . Gallant , B . O . Patrick and M . J . Maclachlan , J . Org Chem ., 69(25), 8739 – 8744 , 2004 .

7. I . J . Patel and S . J . Parmar , E – Journal of Chemistry 7(2) , 617 – 623 , 2010 .
8. Selvam P. , Chandramonan M. , Dclercq E., Witrrouw M. and Pannecouque C. , Eur . J .Pharm Sci , 14(4) , 313 – 316 , 2001 .
9. More P. G. , Bhalvankar R. B. and Pattar S. C. , J . Indian Chem Soc ., 78, 474 – 475 , 2001 .
10. Bayer E. , Chem. Ber ., 90(10) , 2325 – 2338 , 1957 .
11. Chambhare R. V. , Khadse B. G. , Bobde A. S. and Bahekar R. H. , Eur. J. Med. Chem ., 38(7), 89 – 100 , 2003 .
12. Rathelot P. , Azas N. , El – Kashef H. and Delmas F. ,Eur . J . Med . Chem ., 37(8), 671- 679 , 2002 .
13. Holla B. S. , Malini K. V., Roa B. S. , Sarojini B. K. and Kumari N. S. , Eur. J . Med . Chem ., 38(7), 313 – 318 , 2003 .
14. Holla B. S., Veerendra B. , Shivananda M. K. and Poojary B. , Eur . J . Med . Chem ., 38(7), 759 - 767 , 2003.
15. Jarrahpour A. , Khalili D. , Clereq E. D. , Salmi C. and Michel J. , Molecules , 12 ,1720 -1730 ,2007 .
16. Toggi A. E. , Hafez A. M. , Wack H. , Young B. and Lectka D. , J. Am. Chem. Soc. , 124, 6626 - 6635 , 2002 .
17. Jumat S. , Nadia S. , Int. J. Pharm. Tech. Research. 2(1), 205 – 208 , 2010 .
18. M. M. Sprung, Chem. Rev., 26,297, 1940 .

تحوير الكوبوليمر كلوريد الفنايل إلى قاعدة شيف

انعام فاضل موسى محمد

جامعة بغداد / كلية العلوم للبنات /قسم الكيمياء

الخلاصة :

تضمن هذا البحث تحوير الكوبوليمر كلوريد الفنايل الى قواعد شيف وذلك بتحويل الكوبـــوليمر كلوريد الفنايل الى كوبوليمر كلوريد الفنايل هيدرازين وذلك بمفاعلته مع الهيدرازين ومن ثم دخول هذا المشتق بتفاعل تكثيفي مع الديهايدات وكيتونات مختلفة (اليفاتية واروماتية) لينتج قواعد شـــيف . تـــم اثبات التراكيب عن طريق قياس SofteningPoint وقياس اللزوجة وعن طريق قياس FT-IR لها.