

Free radical polymerization of some new vinylic compounds
bearing both ester and amide groups
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Summary

Many vinylic monomers bearing both ester and amide groups were synthesized , starting from amic acids . The resulted monomers were polymerized by free radical method . Full analysis of the prepared compounds were carried out using spectroscopic methods in addition to the physical properties of those compounds .

الخلاصة

تم تحضير العديد من المونيمرات الفايينيلية الحاملة لكلا مجاميع الاستر و الامايد ابتداء من احماض الاميك . بلمرة المونيمرات الناتجة بطريقة الجذور الحرة . ثم اجري تحليل شامل للمركبات المحضرة اعتمادا على الطرق الطيفية بالاضافة الى ايجاد الخواص الفيزيائية لها .

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Introduction

Polyamide plastics have good mechanical, thermal and electrical properties, and can be easily processed⁽¹⁾. Typical engineering plastics include poly amides and poly esters. Compared to poly ester of a similar structure, poly amides have a high glass transition and melting temperature and crystallize more rapidly^(2,3). The disadvantage of poly amides is that they have a high water absorption⁽⁴⁾. Thus it would be of interest to combine the good properties of both the poly esters and poly amides in to copolyesteramides, which gives them the properties intermediate^(5,6). Their rigidity caused by the double bond character of the amide group coupled with extensive hydrogen bonding influences ordering of poly ester amides⁽⁷⁻⁹⁾.

Experimental part

A- Instruments

- 1- melting points were determined on capillary melting point apparatus, Thomas Hoover model 6427-Fio.
- 2- softening points were determined on thermal microscope (Kofler-method) Reichert thermovar.
- 3- infrared spectra were record using solid KBr disk on perkin-Elmer 137A spectrophotometer.
- 4- Elemental analysis were performed by the college of science, university of Mosul (1998-1999).

B- Chemicals or materials

- 1- All chemical were purchased from fluka, BDH and Aldrich.
- 2- Benzene, sodium wire was added to benzene and left for over night, the mixture was then distilled over sodium.
- 3- Azobisisobutyronitrile (AIBN): crystallization from methanol dried under vacuum at room temperature and stored in dark bottle.

Synthesis of maleamic acid (I)

Literature procedures were followed in the preparation with minor modification⁽⁵⁻⁸⁾.

To a slurry of 0.98 (0.01mole) of maleic anhydride in 50ml benzene, a solution of 0.93g(0.01 mole) aniline was added drop wise from dropping funnel and stirring for one hr. The N-phenylmaleamic acid was precipitate, and purified by dissolving in sodium bicarbonate solution and re precipitation with dil.HCl.

All other re preparations maleamic acids are prepared in the same method, the IR and melting point are in agreement with literature⁽⁵⁻⁸⁾.

Synthesis of 3-undecane-4-benzylchloride⁽⁹⁾ (II)

Literature procedure were followed in the preparation with minor modification in two steps:

Step one: synthesis of paraformaldehyde by evaporation of an aqueous solution of (37%) formalin, an amorphous white is produced.

Step two: into a 250ml three necked flask, equipped with reflux, a mechanical stirrer and agas lead-in tube extending to near the bottom flask, place (23.3g, 0.1mole of 3-undecanbenzene, (3g,0.1mole) paraformaldehyde and 3g of finely anhydrous zinc chloride. Support the flask on water bath. Heat the bath to 60C and pass in a rapid steam of hydrogen chloride until no more gas is absorbed cab out 20 minutes); continuous to stirring at 80C about three hours, allow to cool to room temperature, the white oily precipitate wash the product with 50 ml of cold water several time, decantation of water, and left in oven (40C)for

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seven hours. The white oil were put in refrigerator five hours. The sample allowed to heat by hand until the white precipitate is formed. 60% yield were obtained, (m.p 13.0C)

Synthesis of 3-undecane-4-benzyl-N-aryl maleamate general procedure (III)

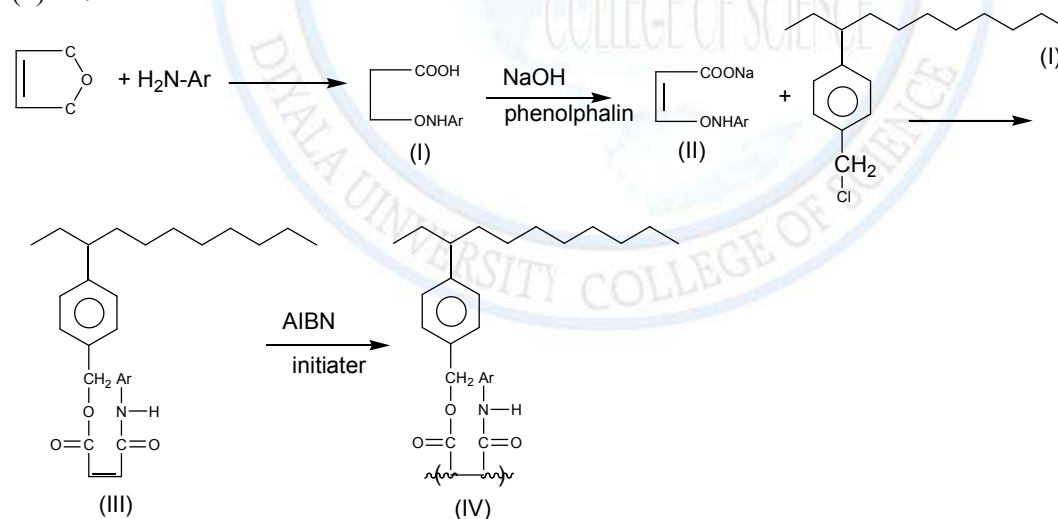
Dissolve or suspend 0.5g of the amic acid in 5ml of water added a drop or two of phenolphthalein indicator, and then 5% sodium hydroxide unit the acid is just neutralized. Add few drop of hydrochloric acid so that the final solution is faintly acid (litmus). Introduce 0.5 of 3-undecane-4-benzyl chloride dissolved in 5ml of rectified or methylated spirit and heat the mixture under reflux for 1 hr. Allow the solution to cool, filter the separated preprecipitate. Recrystallise by dissolve the solid in hot alcohol, added light naphtha until the white precipitate is formed.

Homopolymerization of 3-undecane-4-benzyl-N-aryl maleamate (IV)

In the polymerization bottle, the nine grams of titled monomer was dissolved in 20ml of freshly distilled THF solvent. To this solution added 0.02g of AIBN initiator. Purged with dry nitrogen before heating at 66-70 C. on a water bath for three hours. The resulting clear solution was added to a 250ml of methanol. The white precipitation was formed and purified by dissolving in acetone and re precipitation with petroleum ether, according to G.Odian method⁽¹⁰⁾.

Results and Discussion

It is well known a substituted primary amine is reacted easily with cyclic anhydride to produce amic acid (I). The poly vinylic amic acid, is not seen in the literature. Any amic acid compound have both a carboxylic acid and amide functional group. When allowed carboxylic group (in amic acids) to react with 3-undecane benzyl chloride in aqueous base, the ester group was formed beside the amide. The synthesis of these compounds is presented in scheme (1).



Scheme(1) : Acts Steps of synthesis vinylic compound containing both ester-amide group(III) and their polymerization (IV)

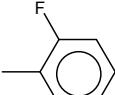
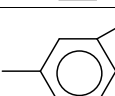
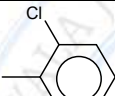
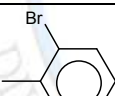
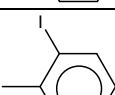
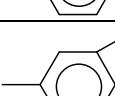
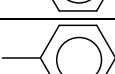
The IR spectra of these compounds (III) showed the characteristic absorption of ester group at $(1748-1763)cm^{-1}$, amide group $(1684-1693)cm^{-1}$, (C-H) olefinic group at $(3024-3035)cm^{-1}$, and (C=C) at $(1605)cm^{-1}$. The increasing absorption of carboxylic group, in the compound (III) and dissolved in sodium bicarbonates solution indicated esterification is formed and beside these facts the elemental analysis was fitted with structural formulae (III) (see table3). Homopolymerization of the above (III) have been synthesized through free radical method in

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the presence of AIBN initiator and benzene as solvent, the polymer (IV) have higher melting point than the corresponding monomers (III) and the absence of double bond in IR spectrum and the remain red color when addition bromine solution or violet color when addition KMnO_4 solution to these compound (IV).

Table (1) : % yield ,color,melting point (C) of new vinylic-esters-amides compounds (III)

Code#	Ar	% yield	color	M.p.C
1		83	White	113
2		79	White	127
3		80	White	130
4		76	white	137
5		75	White	143
6		79	White	197
7		81	White	152
8		77	Pale yellow	162
9		76	Pale yellow	164
10		74	Pale yellow	171
11		78	White	175
12		76	White	178
13		75	white	183

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Table(2) : IR absorptions and elemental analysis –ester-amides compounds(III)

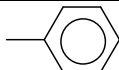
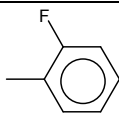
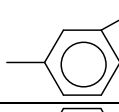
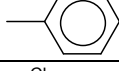
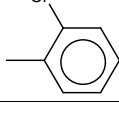
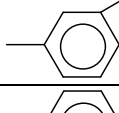
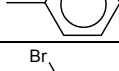
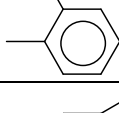
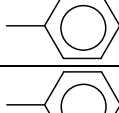
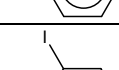
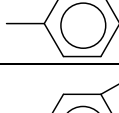
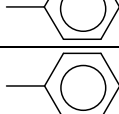
Code#	ν_{NH}	IR (KBr)cm-1		$\nu_{\text{C=O}}$ ester $\nu_{\text{C=O}}$ amide	$\nu_{\text{C-O}}$	M.wt Formula	Elemental analysis calcd (found)		
		Aromatic Aliphatic	Olefenic $\text{CH}_3, \text{CH}_2, \text{CH}$				%C	%H	%N
1	3450	3015	3032 2985,2953,2890	1764 1693	1191	$\text{C}_{28}\text{H}_{36}\text{O}_3\text{N}=434$	77.42 77.39	8.29 8.21	3.23 3.19
2	3447	3017	3025 2980,2950 ,2896	1759 1684	1188	$\text{C}_{28}\text{H}_{35}\text{O}_3\text{NF}$			
3	3448	3021	3034 2990,2954,2899	1754 1687	1175				
4	3449	3018	3028 2995,2953, 2900	1754 1690	1173	$\text{C}_{28}\text{H}_{35}\text{O}_3\text{NF}=452$	74.34 74.31	7.74 7.72	3.09 7 3.08 5
5	3448	3020	3033 2995,2950 ,2898	1750 1688	1190				
6	3451	3025	3035 2993,2948, 2891	1748 1685	1177				
7	3454	3017	3028 2990,2950,2890	1750 1690	1180	$\text{C}_{28}\text{H}_{35}\text{O}_3\text{NCl}$	71.72 71.70	7.47 7.41	2.99 2.93
8	3450	3015	3024 2994,2948 ,2880	1752 1693	1187				
9	3455	3017	3025 2993,2953 ,2890	1754 1687	1184				
10	3447	3018	3027 2995,2952,2890	1750 1680	1170				
11	3444	3016	3028 2992,2950,2889	1750 1684	1175				
12	4447	3018	3027 2990,2948 ,2895	1754 1690	1184				
13	4448	3017	3026 2995,2951,2888	1750 1688	1177				

* the numbering as in table (1)

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Table (3) : IR absorptions, softening points , % conversions and intrinsic viscosity of the new poly(vinylic –ester-amides)

Code#	Ar	νN-H	IR (KBr)cm-1	νC=O ester νC=O amide	νC-O	S.p.	%Conversion	ηint .
			νC-H aromatic νC-H aliphatic CH ₃ ,CH ₂ ,CH					
14		3500	3018 2987,2951,2889	1757 1698	1195	203-204	67	0.45
15		3480	3015 2982,2952,2900	1760 1686	1190	211-213	65	0.51
16		3450	3018 2993,2957,2900	1756 1690	1180	219-222	66	0.55
17		3448	3019 2995,2955,2899	1756 1687	1185	226-228	64	0.59
18		3485	301 2990,2950,2900	1755 1686	1177	241-244	67	0.63
19		3493	3018 2993,2952,2893	1756 1687	1178	250-251	70	0.68
20		3492	3017 2996,2961,2901	1759 1690	1187	261-263	69	0.69
21		3495	3018 2991,2952,2889	1754 1690	1185	270-272	73	0.71
22		3496	3018 2993,2951,2889	1753 1691	1187	274-278	71	0.78
23		3495	3018 2992,2951,2889	1754 1691	1186	279-281	73	0.76
24		3500	3017 2995,2950,2901	1752 1690	1186	284-286	71	0.77
25		3498	3017 2996,2951,2900	1753 1690	1185	288-291	70	0.78
26		3500	3018 2996,2951,2900	1754 1685	1188	295-298	69	0.79

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