

# Synthesis of Novel N,N-disubstituted Maleamic Esters and Their Applications as Plasticizers for Poly vinylchloride

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## Abstract

Three N,N-Substituted Bis maleamic acids were prepared in high yields (91-94)% from reaction of maleic anhydride with o-phenylenediamine , ethylenediamine and thiourea. The corresponding Esters were prepared in high yields (85-92)% from reaction of the prepared N,N-Substituted bis maleamic acids with methanol and isopropanol.

The prepared esters were tested as plasticizers for poly(vinyl chloride) and comparison the results with (DOP) and (DBP) the universal plasticizers for PVC indicated that the prepared esters in general had high plasticization efficiency.

## Introduction

The ability of PVC to tolerate large amounts of plasticizers, fillers and other additives is unique among the thermoplastics and has made it possible to develop a wide range of properties in flexible PVC<sup>(1-3)</sup>.

This versatility coupled with attractive economics has been responsible for the growth of flexible PVC over the years<sup>(4,5)</sup>.

Thus, in recent decades extensive research efforts have been directed towards the preparation and application of new plasticizers for PVC<sup>(6-9)</sup> since plasticizers are efficient additives in modification of polymers to desired physical and mechanical properties. Plasticized compositions now represent more than (95%) of the total usage of PVC polymer and PVC applications consume approximately more than (80%) of total plasticizers production.

In the present work six N,N-substituted bis maleamic esters were prepared from the corresponding N,N-substituted bis maleamic acids via esterification reaction using different alcohols in the presence of concentrated sulfuric acid.

The new esters were tested as plasticizers for PVC plastic and in general they show good plasticizing activity.

## Experimental

Melting points were determined on Gallen Kamp Capillary melting point apparatus and were uncorrected. IR spectra were recorded on Shimadzu FTIR-8300 Fourier Transform Infrared Spectrophotometer. Softening points were determined on Thermal Microscope Reichert Thermovar, SP1, 160. and U.V.

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spectra were recorded on Shimadzu UV-Vis recorder spectrophotometer.

### **Preparation of N,N-Substituted bis maleamic Acids [1-3]**

Thiourea, ethylene diamine and o-phenylene diamine were allowed to react with maleic anhydride according to literatures<sup>(10)</sup>. The prepared bis amic acids were purified by recrystallization from ethanol.

Table (I) lists melting points, percent yields and major IR absorptions of the prepared amic acids

### **Preparation of N,N-substituted bis maleamic esters:**

#### **Esterification of the prepared bis amic acids with methanol [4-6]**

The titled compounds were prepared according to literature procedures<sup>(11,12)</sup> with few modifications: In a (50 ml) round bottomed flask fitted with a pressure-equalized funnel was dissolved (0.001 mole) of N,N-substituted bis maleamic acids in (20 ml) of methanol. To the resulted solution few drops of concentrated sulfuric was added with stirring and reflux the mixture for (4 hrs). The solvent was evaporated to produce a thick oil which was recrystallized from petroleum ether b.p. (60-80)°C. Table (II) lists melting points, percent yields, U.V. data and major IR absorptions of the prepared esters.

#### **Esterification of the prepared bisamic acids with isopropanol [7-9]**

The same procedure used in the preparation esters (4-6) was followed in the preparation of the titled compounds except using of isopropanol instead of methanol.

The prepared esters were purified by recrystallization from petroleum ether b.p. (60-80)°C. Percent yields, melting points, U.V. data and major IR absorptions of the prepared esters are listed in Table (III).

### **Testing of The Prepared Esters as Plasticizers for PVC**

Four samples of each ester were prepared by mixing and grinding a constant weight (1 gm) of poly(vinyl chloride) PVC with four different weights of the prepared ester (plasticizer) (0.1, 0.2, 0.3 and 0.4 gm) respectively.

Softening points for all the prepared twenty four samples were recorded on (Thermal Microscope) apparatus using slides prepared from the plasticized samples.

In the same manner another eight samples were prepared by using dioctylphthalate (DOP) in four of them and dibutylphthalate (DBP) in the others as plasticizers. Softening points of the later eight samples were also determined and the results were used for comparison.

All the results and details of this study are listed in Table (IV).

### **Results and Discussion**

Many esters are reported to have high efficiency in plasticization of PVC plastic to modify the polymer to desired physical and mechanical properties<sup>(13,14)</sup> so the target of this work is to synthesize new esters and testing their ability for

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plasticization of PVC. Preparation of the new esters includes two steps, in first step three N,N-substituted bis maleamic acids were prepared from reaction of one mole of thiourea, ethylene diamine and o-phenylene diamine with two mole maleic anhydride according to literature procedures<sup>(10)</sup> and excellent yields of crystalline amic acids were resulted in all cases.

In the second step of this work the prepared N,N-substituted bis maleamic acids were converted to the corresponding esters by allowing them to react with methanol and isopropanol respectively in the presence of concentrated sulfuric acid.

Tables (I), (II) and (III) list melting points, percent yields, U.V.  $\lambda_{\max}$  and major IR absorptions of the prepared compounds.

It is noticeable that IR spectra of the prepared N,N-substituted bis maleamic acids revealed band in the region (3235-3260)  $\text{cm}^{-1}$  due to stretching vibration of amidic (N-H) groups, and clear band in the region (1690-1720) due to stretching vibration of carboxylic (C=O) groups. IR spectra of the prepared esters revealed a clear band in the region (1705-1720) due to stretching vibration of esteric (C=O) groups.

U.V. spectra of the prepared esters revealed absorptions at wavelengths (256-331) nm these absorptions were assigned to  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  transitions in double bond which was in conjugation with two carbonyl groups in ester moiety.

Some IR and U.V. spectra of the prepared esters are shown in Figure (1) to (3). In fact this work has been directed towards synthesis of new esters and testing their ability for plasticization of PVC, thus the final step of this work includes testing the ability of the prepared esters as plasticizers for PVC plastic.

Twenty four samples were prepared and their softening points were recorded. The results showed that the prepared esters caused a clear depression in PVC softening point and the depression increased with increasing of plasticizer concentration.

In general type and content of plasticizer effected on several physicochemical properties of PVC<sup>(15)</sup>, thus plasticized PVC showed lower softening points due to the formation of secondary molecular forces between plasticizer molecules and polymeric chains especially when there is a good compatibility between them.

These new forces will reduce molecular forces between the polymer chains themselves and this will decrease the orientation of the crystalline phase which inturn reduce stiffness, softening points and tensile strength since these mechanical properties are influenced by degree of crystallinity<sup>(16,17)</sup>.

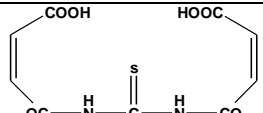
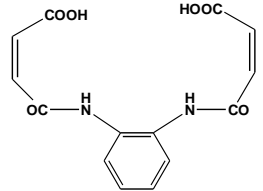
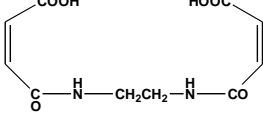
Plasticization efficiency of the prepared plasticizers were tested by comparison the results with (DOP) and (DBP) the universal plasticizers for PVC.

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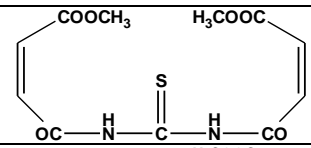
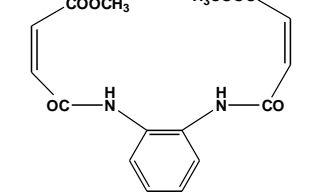
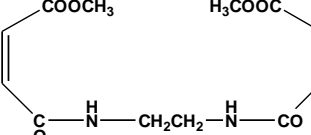
The results showed that all the prepared esters in this work have high plasticization efficiency for PVC and they are more efficient than both (DOP) and (DBP).

All the results of this study are listed in Table (IV) while softening curves of the prepared esters are shown in Figures (4) and (5).

**Table (I): Melting points, percent yields and spectral data of bis amic acids**

Comp. No.	Compound structure	Color	Yield%	Melting point °C	U.V. $\lambda_{max}$	Major IR absorptions, $cm^{-1}$			
						$\nu_{N-H}$	$\nu_{C=O}$ carboxylic	$\nu_{C=O}$ amide	$\nu_{C=C-H}$
1		yellow	91	241-243	248	3260	1720	1660	2939
2		green	94	216-218	324	3240	1700	1625	3120
3		yellow	92	206-208	327	3235	1690	1630	3115

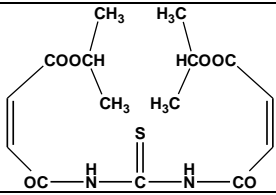
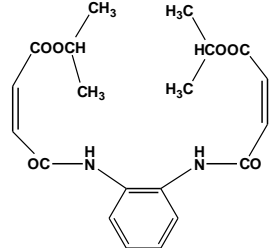
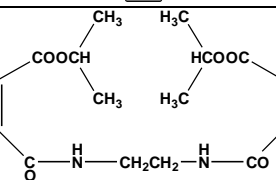
**Table (II): Physical properties and spectral data of the prepared esters**

Comp. No.	Compound structure	Yield %	Melting point °C	U.V. $\lambda_{max}$	Major IR absorptions, $cm^{-1}$			
					$\nu_{N-H}$	$\nu_{C=O}$ Ester	$\nu_{C=O}$ Amide	$\nu_{C-O}$ Ester
4		87	Oil	256	3122	1720	1654	1124
5		89	71	329	3313	1716	1635	1172
6		92	Oil	330	3398	1708	1635	1176

**Table (III): Physical properties and spectral data of the prepared esters**

Comp.	Compound structure	Yield	Melting	U.V.	Major IR absorptions, $cm^{-1}$
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No.		%	point °C	λ <sub>max</sub>	νN-H	νC=O Ester	νC=O Amide	νC-O Ester
7		85	52	260	3377	1716	1701	1149
8		86	Oil	331	3311	1708	1635	1172
9		88	Oil	329	3410	1705	1629	1174

**Table (IV) Effect of different weight ratios of plasticizers on PVC softening point**

Comp. No.	Weight ratio of plasticizer to (1gm) of PVC	Softening point °C
4	0.1	132-144
	0.2	120-129
	0.3	103-114
	0.4	94-101
5	0.1	140-156
	0.2	132-143
	0.3	118-130
	0.4	98-108
6	0.1	113-121
	0.2	102-110
	0.3	90-95
	0.4	80-88
7	0.1	151-172
	0.2	135-148
	0.3	120-133
	0.4	104-115
8	0.1	141-159
	0.2	126-139
	0.3	112-123
	0.4	100-110
9	0.1	142-162

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	0.2	131-142
	0.3	118-127
	0.4	103-113
DOP	0.1	185-210
	0.2	175-195
	0.3	160-180
	0.4	150-170
DBP	0.1	185-208
	0.2	180-195
	0.3	165-187
	0.4	150-170

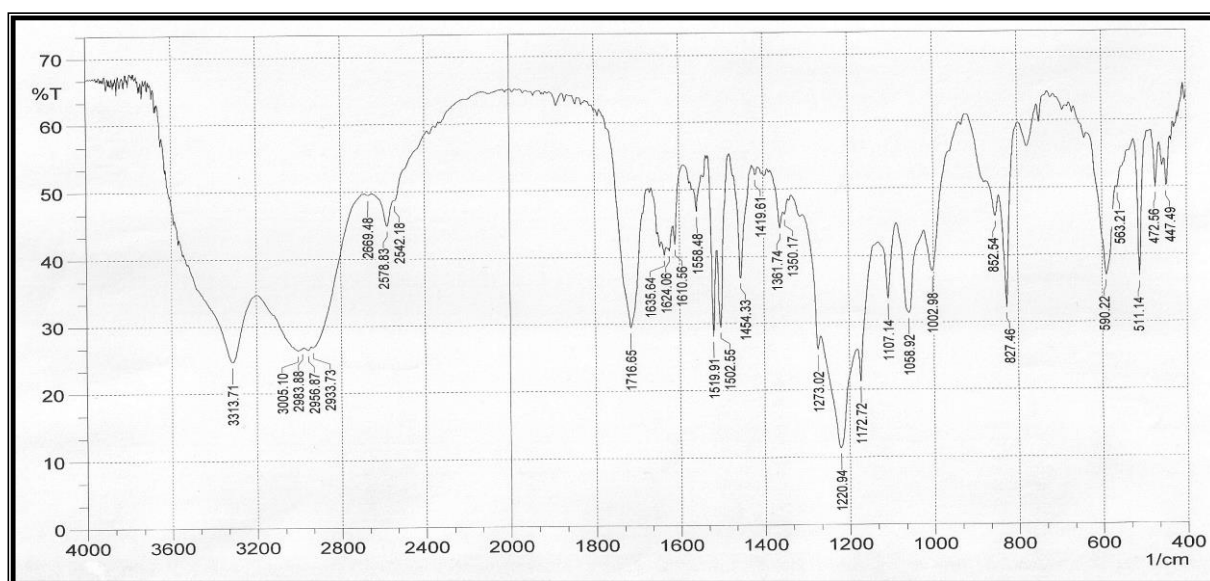


Fig.(1) IR spectrum of compound (5).

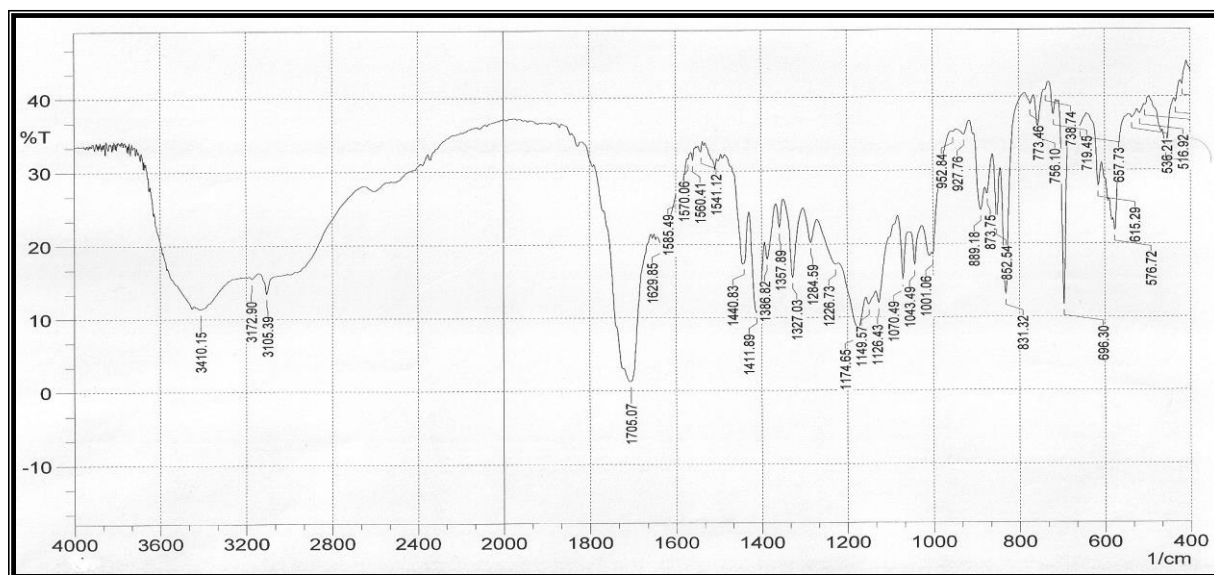


Fig. (2) IR spectrum of compound (9).

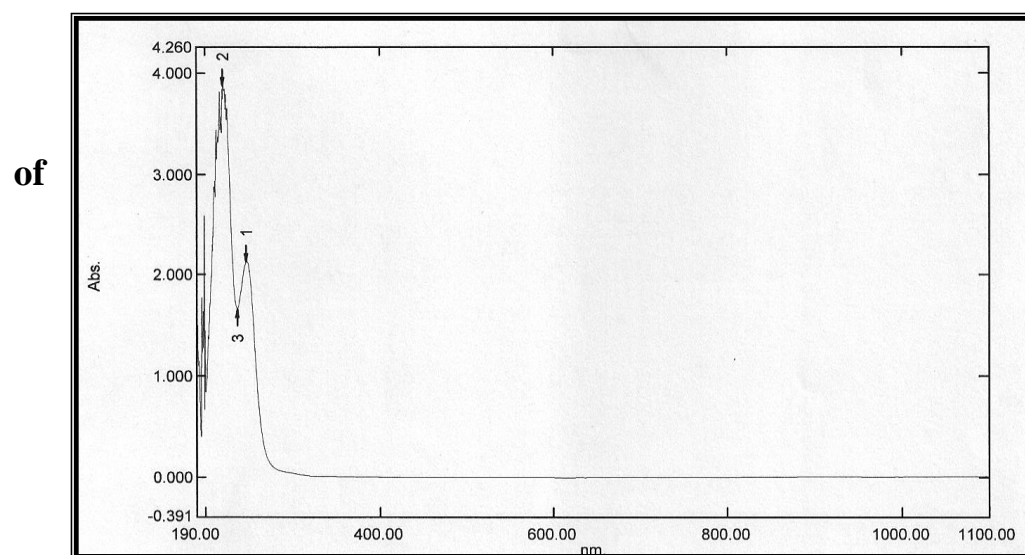


Fig.(3)  
UV  
spectrum

compound (1)

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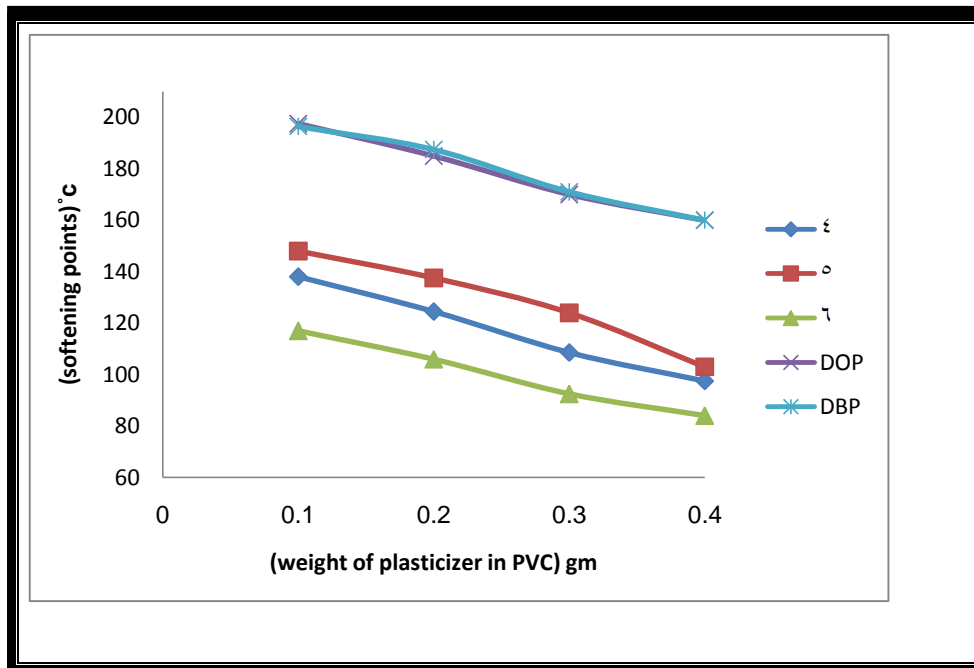


Fig.(4) softening curves of (4-6) esters compared with (DOP) and (DBP)

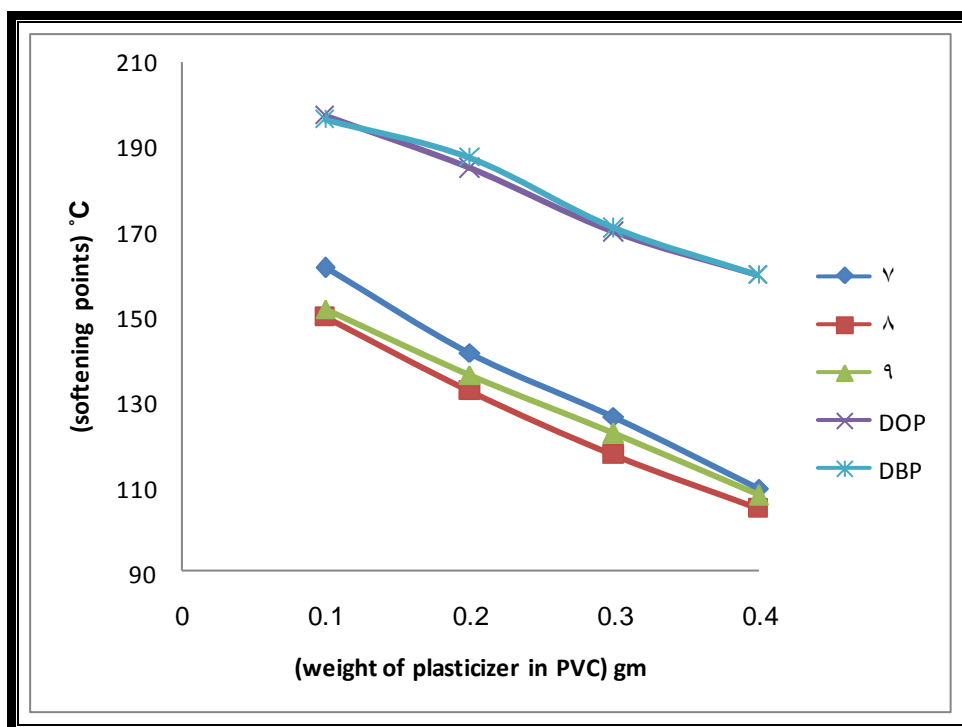


Fig.(5) softening curve of esters(7-9) compared with (DOP) and (DBP)



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## الخلاصة

تضمن البحث تحضير ثلاثة من حوامض N,N-معوض ثنائي مالي اميك بمنتوج عالي قدره (91-94)% وذلك من تفاعل مركبات اورثوفنلين ثنائي الامين، اثلين ثنائي الامين و الثايوريا مع انهيدريد المالك.

تم تحضير الاسترات المقابلة بمنتوج عالي قدره (85-92)% وذلك من تفاعل حوامض N,N-معوض ثنائي مالي اميك المحضرة مع الميثانول و الايزوبروبانول .

ان الهدف الرئيسي من هذا البحث هو تحضير استرات جديدة واختبار كفاءتها كملدنات لبولي (كلوريد الفايثيل) PVC وعلى هذا الاساس فقد تضمن الجزء الاخر من البحث اختبار قابلية الاسترات المحضرة على تليدين PVC وقد تم ذلك من خلال اعداد اربعة وعشرون نموذج من PVC مع الاسترات المحضرة وفق نسب وزنية معينة ثم سجلت درجات التلين لجميع هذه النماذج. لقد اوضحت النتائج بان اضافة الاسترات المحضرة الى PVC تحدث انخفاضاً واضحاً في درجة تلين البوليمر ويزداد الانخفاض مع زيادة تركيز الاستر (الملدن) في النموذج.

اما لغرض التعرف على كفاءة التلين للاسترات المحضرة فقد تمت مقارنة النتائج المستحصلة مع النتائج في حالة استخدام الملدنات العالمية لبولي (كلوريد الفايثيل) وهما (DOP) و (DBP) على التوالي وقد اظهرت نتائج المقارنة بان الاسترات المحضرة عموماً ذات كفاءة عالية في تليدين PVC.