

Synthesis of Novel N-Substituted Phthalimidyl Esters and Their Applications as Plasticizers for Poly (Vinyl Chloride)

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Date of acceptance 3/12/2006

Abstract

Three N-(hydroxyphenyl) phthalamic acids were prepared in high yields (92-95)% from reaction of phthalic anhydride with o,m and p-aminophenols.

Dehydration of the prepared phthalamic acids by fusion produced good yields (86-90)% of the corresponding N-(hydroxyphenyl)phthalimides. The prepared phthalimides were esterified to the corresponding methacrylates, benzoates and cinnamates in good yields via their treatment with different acid chlorides in the presence of triethylamine.

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⁽¹⁻³⁾.

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

Thus, in recent decades extensive research efforts have been directed towards the preparation and application of new plasticizers for PVC⁽⁶⁻⁹⁾ since plasticizers are efficient additives in modification of polymers to desired physical and mechanical properties.

In the present work nine novel N-substituted phthalimidyl esters were prepared from the corresponding N-(hydroxyphenyl)phthalimides via esterification reaction using different acid chlorides in the presence of triethylamine.

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. U.V. spectra were recorded on Shimadzu UV-Vis recorder spectrophotometer U.V. 160. and C.H.N. analyses were determined by Perkin-Elmer 240 element analyzer.

1- Preparation of N-(Hydroxyphenyl)phthalamic Acids [1-3]

Ortho, meta and p-aminophenols were allowed to react with phthalic anhydride according to literatures⁽¹⁰⁾. The prepared amic acids were purified by recrystallization from ethanol.

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

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2- Preparation of N-(Hydroxyphenyl)phthalimides [4-6]

The titled compounds were prepared by dehydration of the corresponding amic acids according to literature procedures⁽¹¹⁾ using fusion method. The resulted product was purified by recrystallization from cyclohexane. Melting points, percent yields, U.V. data and major IR absorptions of the prepared phthalimides are listed in Table (II).

3- Preparation of N-phthalimidylphenyl methacrylate [7-9]

The titled compounds were prepared according to literature procedures^(12,13) with few modifications:

In a (250 ml) round bottomed flask fitted with a pressure-equalized funnel was dissolved (0.01 mole) of N-(hydroxyphenyl)phthalimide in (40 ml) of dry acetone.

To the resulted solution triethylamine (0.01 mole) was added followed by dropwise addition of methacryloyl chloride (0.01 mole) with stirring and cooling then stirring was continued for another (7 hrs) before filtration.

The filtrate was evaporated under reduced pressure and the residue was extracted with chloroform and water for three times. The organic layer was dried and the solvent was evaporated to produce a thick oil which was recrystallized from petroleum ether b.p. (60-80)°C.

Table (III) lists melting points, percent yields, U.V. data and major IR absorptions of the prepared methacrylate esters.

4- Preparation of N-phthalimidylphenyl Benzoates [10-12]

The same procedure used in the preparation of methacrylate esters was followed in the preparation of the titled compounds except using of benzoyl

chloride instead of methacryloyl chloride.

The prepared benzoate 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 benzoate esters are listed in Table (IV).

5- Preparation of N-phthalimidylphenyl Cinnamates [13-15]

The same procedure used in the preparation of methacrylate esters was followed in the preparation of the titled compounds except using of cinnamoyl chloride instead of methacryloyl chloride.

The prepared cinnamate 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 cinnamate esters are listed in Table (V).

6- 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 thirty six 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 (VII).

Results and Discussion

In continuation of our research program directed towards the synthesis of novel imidyl esters having high plasticization efficiency for PVC plastic, a new series of phthalimidyl esters including benzoates, methacrylates and cinnamates has been prepared.

Preparation of the new esters includes many steps, in first step three N-(hydroxyphenyl)phthalamic acids were prepared from reaction of equimolar amounts of o,m and p-aminophenols with phthalic anhydride according to literature procedures⁽¹⁰⁾ and excellent yields of crystalline amic acids were resulted in all cases. Dehydration and cyclization of the prepared phthalamic acids gave the corresponding N-(hydroxyphenyl)phthalimides.

Dehydration was achieved by using fusion method since the use of (acetic anhydride-sodium acetate anhydrous) as dehydrating agent caused esterification of phenolic hydroxyl groups and produced acetylated phthalimides instead of the desired

N-(hydroxyphenyl)phthalimides.

In the third step of this work the prepared phthalimides were converted to the corresponding methacrylate, benzoate and cinnamate esters by allowing them to react with methacryloyl, benzoyl and cinnamoyl chlorides respectively in the presence of triethylamine.

Tables (I), (II), (III), (IV) and (V) list melting points, percent yields, U.V. λ_{max} and major IR absorptions of the prepared compounds while C.H.N. analysis of some of them are listed in Table (VI).

It is noticeable that IR spectra of the prepared phthalimides revealed a clear band in the region (3321-3412) cm^{-1} due to stretching vibration of phenolic (O-H), thus success of

esterification reaction of these imides with different acid chlorides is confirmed by disappearance of (O-H) absorption band in IR spectra of the prepared esters.

U.V. spectra of the prepared esters revealed absorptions at wavelengths (290-305) nm these absorptions were assigned to $\pi \rightarrow \pi^*$ transitions in benzene ring which was in conjugation with two carbonyl groups in phthalimidyl moiety and $\pi \rightarrow \pi^*$ transition benzene ring which was in conjugation with attached benzoate or methacrylate or cinnamate groups.

IR and U.V. spectra of the prepared esters are shown in Figure (1) to (6).

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.

Thirty six 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⁽¹⁴⁾, 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^(15,16).

Plasticization efficiency of the prepared plasticizers were tested by comparison the results with (DOP) and

(DBP) the universal plasticizers for PVC.

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 (VII) while softening curves of the prepared esters are shown in Figures (7) to (9).

Table (I): Melting points, percent yields and spectral data of phthalamic acids



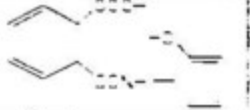
| Comp No. | Compound structure | Yield% | Melting point °C | U.V. λ_{max} | Major IR absorptions, cm^{-1} | | | | |
|----------|---|--------|------------------|----------------------|---------------------------------|-----------|----------------------|-----------------|--------------------|
| | | | | | ν O-H | ν N-H | ν C=O carboxylic | ν C=O amide | ν C-H Aromatic |
| 1 |  | 85 | 294-295 | 277 | 3250 | 3100 | 1700 | 1650 | 3090 |
| 2 |  | 82 | 212-213 | 289 | 3350 | 3200 | 1700 | 1625 | 3100 |
| 3 |  | 84 | 227-228 | 268 | 3150 | 3000 | 1690 | 1660 | 3060 |

Table (II): Melting points, percent yields and spectral data of phthalimides

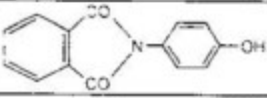
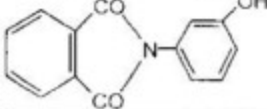
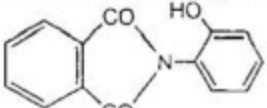
| Comp. No. | Compound structure | Yield% | Melting point °C | U.V. λ_{max} | Major IR absorptions, cm^{-1} | | | |
|-----------|---|--------|------------------|----------------------|---------------------------------|-----------------|-----------|--------------------|
| | | | | | ν O-H phenolic | ν C=O Imide | ν C-N | ν C-H Aromatic |
| 4 |  | 88 | 280-282 | 285 | 3412 | 1714 | 1394 | 3072 |
| 5 |  | 90 | 201-202 | 285 | 3321 | 1707 | 1394 | 3075 |
| 6 |  | 86 | 206-208 | 285 | 3380 | 1699 | 1388 | 3051 |

Table (III): Physical properties and spectral data of N-phthalimidylphenyl methacrylates

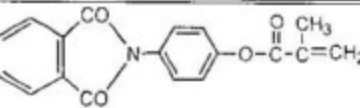
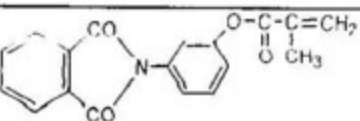
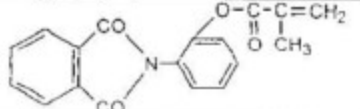
| Comp. No. | Compound structure | Yield% | Melting point °C | U.V. λ_{max} | Major IR absorptions, cm^{-1} | | |
|-----------|---|--------|------------------|----------------------|---------------------------------|-----------------|-----------------|
| | | | | | ν C=O Ester | ν C=O Imide | ν C-O Ester |
| 7 |  | 89 | Oil | 305 | 1760 | 1705 | 1130 |
| 8 |  | 78 | 82-84 | 300 | 1760 | 1734 | 1173 |
| 9 |  | 83 | Oil | 300 | 1770 | 1728 | 1141 |

Table (IV): Physical properties and spectral data of N-phthalimidylphenyl benzoates

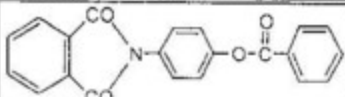
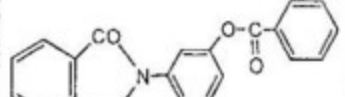

| Comp. No. | Compound structure | Yield% | Melting point °C | U.V. λ_{max} | Major IR absorptions, cm^{-1} | | |
|-----------|---|--------|------------------|----------------------|---------------------------------|-------------------|-------------------|
| | | | | | $\nu_{C=O}$ Ester | $\nu_{C=O}$ Imide | ν_{C-O} Ester |
| 10 |  | 93 | 105-107 | 291 | 1782 | 1689 | 1175 |
| 11 |  | 86 | Oil | 291 | 1770 | 1700 | 1165 |
| 12 |  | 88 | 95-96 | 290 | 1775 | 1710 | 1170 |

Table (V): Physical properties and spectral data N-phthalimidylphenyl cinnamates

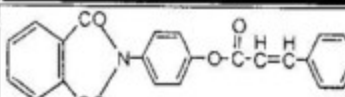
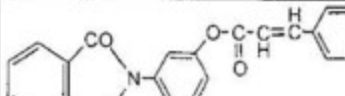
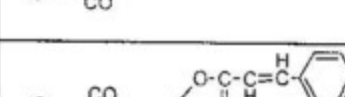
| Comp. No. | Compound structure | Yield% | Melting point °C | U.V. λ_{max} | Major IR absorptions, cm^{-1} | | |
|-----------|---|--------|------------------|----------------------|---------------------------------|-------------------|-------------------|
| | | | | | $\nu_{C=O}$ Ester | $\nu_{C=O}$ Imide | ν_{C-O} Ester |
| 13 |  | 90 | 124-125 | 291 | 1735 | 1705 | 1180 |
| 14 |  | 91 | 78-79 | 290 | 1774 | 1712 | 1134 |
| 15 |  | 84 | Oil | 290 | 1750 | 1705 | 1128 |

Table (VI) C.H.N. Analysis of some of the prepared compounds

| Comp. No. | Calculated | | | Found | | |
|-----------|------------|------|------|-------|------|------|
| | %C | %H | %N | %C | %H | %N |
| 4 | 70.29 | 3.77 | 5.86 | 70.00 | 4.00 | 5.80 |
| 5 | 70.29 | 3.77 | 5.86 | 70.29 | 3.74 | 5.50 |
| 8 | 70.35 | 4.23 | 4.56 | 70.13 | 4.41 | 4.26 |
| 10 | 73.47 | 3.79 | 4.08 | 73.66 | 3.94 | 3.91 |
| 12 | 73.47 | 3.79 | 4.08 | 73.30 | 4.00 | 4.18 |
| 13 | 74.79 | 4.06 | 3.79 | 74.71 | 3.84 | 4.03 |
| 15 | 74.79 | 4.06 | 3.79 | 74.66 | 4.01 | 4.00 |

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

| Comp. No. | Weight ratio of plasticizer to (1gm) of PVC | Softening point °C |
|-----------|---|--------------------|
| 7 | 0.1 | 152-171 |
| | 0.2 | 135-148 |
| | 0.3 | 121-132 |
| | 0.4 | 104-115 |
| 8 | 0.1 | 141-159 |
| | 0.2 | 126-139 |
| | 0.3 | 112-123 |
| | 0.4 | 100-110 |
| 9 | 0.1 | 144-160 |
| | 0.2 | 131-142 |
| | 0.3 | 118-127 |
| | 0.4 | 103-113 |
| 10 | 0.1 | 131-144 |
| | 0.2 | 120-129 |
| | 0.3 | 102-112 |
| | 0.4 | 92-100 |
| 11 | 0.1 | 140-156 |
| | 0.2 | 132-143 |
| | 0.3 | 118-130 |
| | 0.4 | 98-108 |
| 12 | 0.1 | 113-121 |
| | 0.2 | 102-110 |
| | 0.3 | 90-95 |
| | 0.4 | 80-88 |
| 13 | 0.1 | 120-132 |
| | 0.2 | 112-118 |
| | 0.3 | 99-110 |
| | 0.4 | 82-94 |
| 14 | 0.1 | 127-142 |
| | 0.2 | 115-125 |
| | 0.3 | 100-112 |
| | 0.4 | 90-103 |
| 15 | 0.1 | 118-127 |
| | 0.2 | 108-119 |
| | 0.3 | 95-105 |
| | 0.4 | 85-95 |
| 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 |

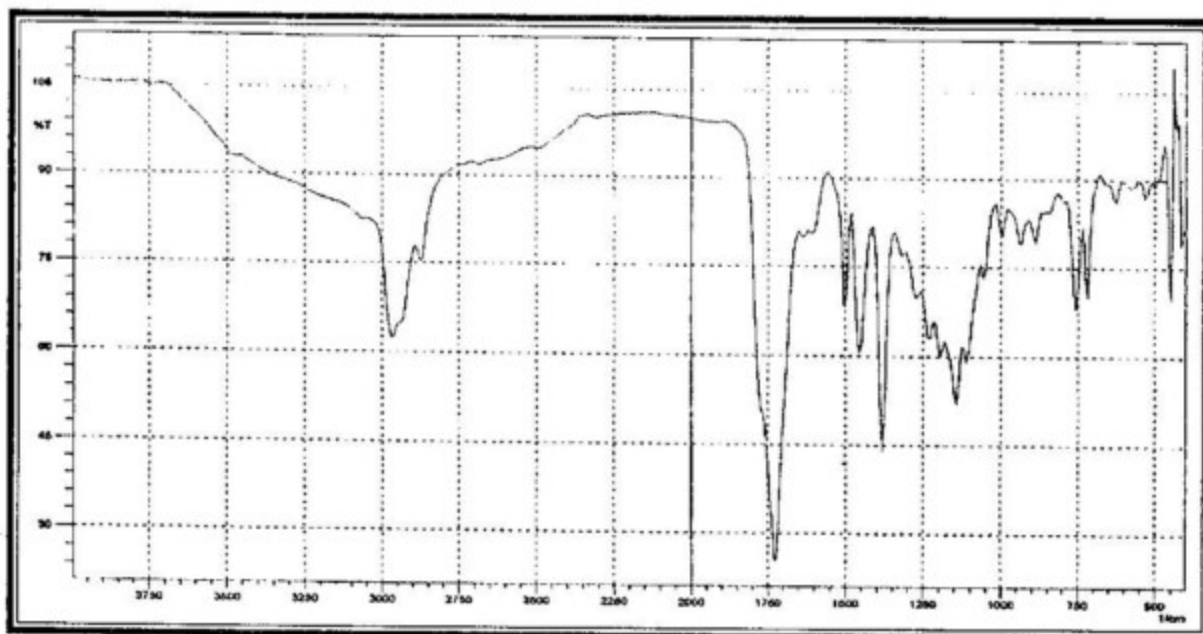


Fig.(1) IR spectrum of compound (9)

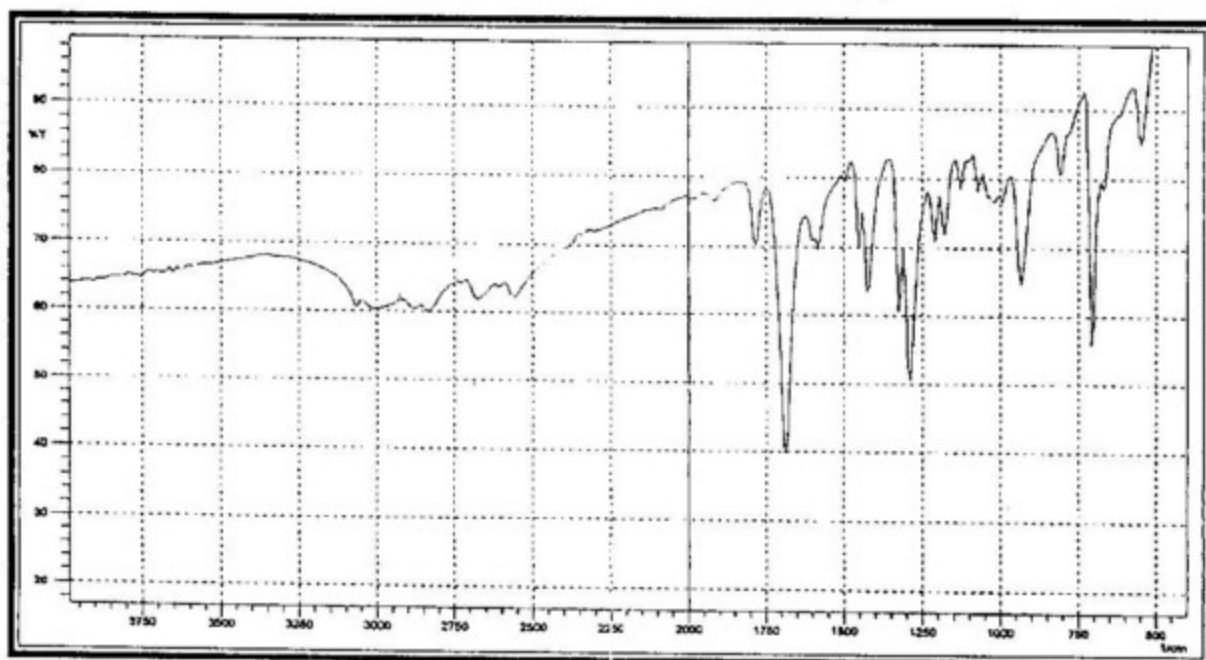


Fig.(2) IR spectrum of compound (10)

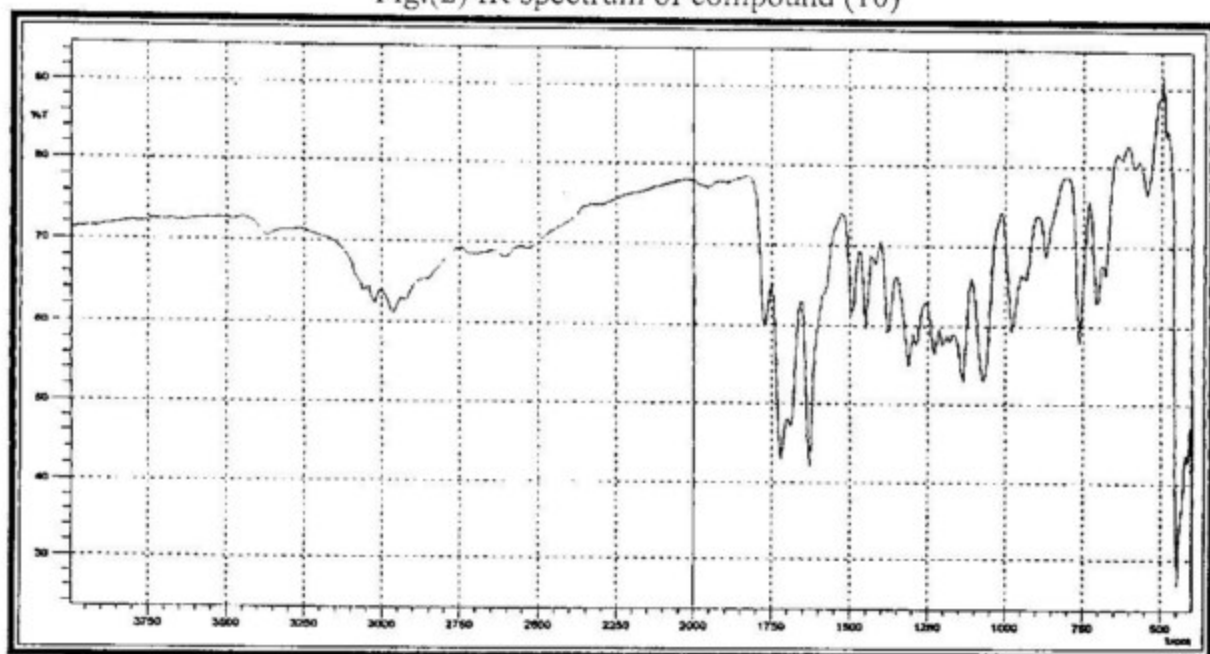


Fig.(3) IR spectrum of compound (14)

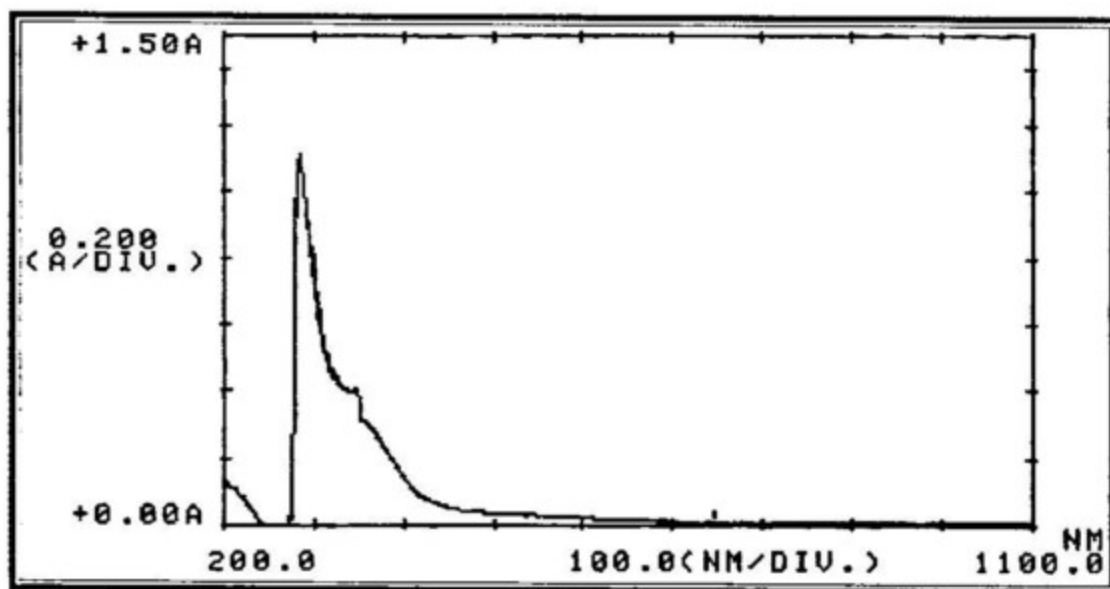


Fig.(4) U.V. spectrum of compound (8)

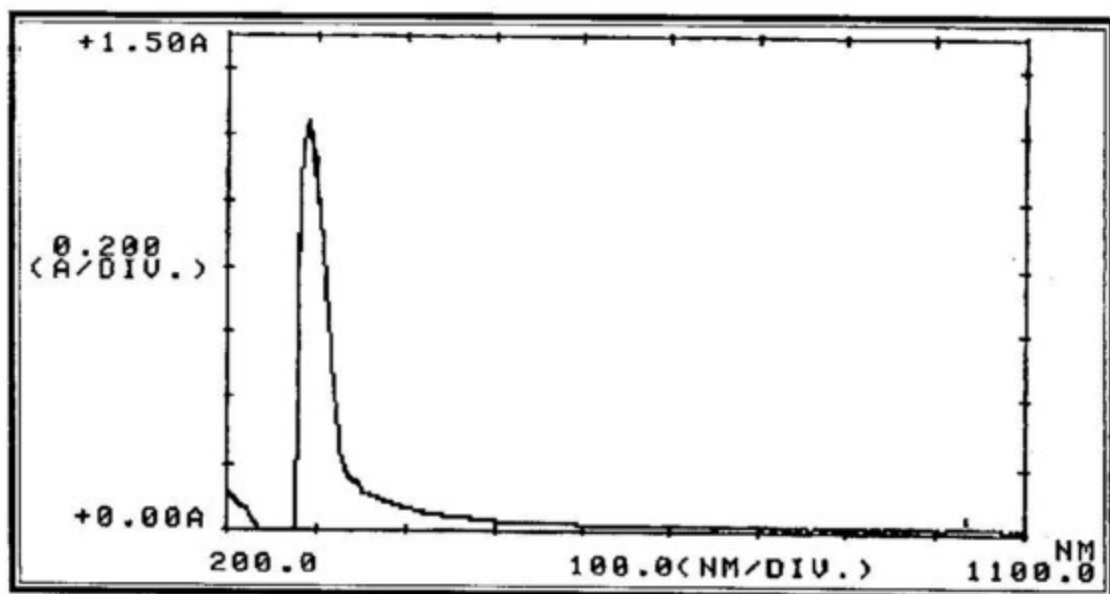


Fig.(5) U.V. spectrum of compound (11)

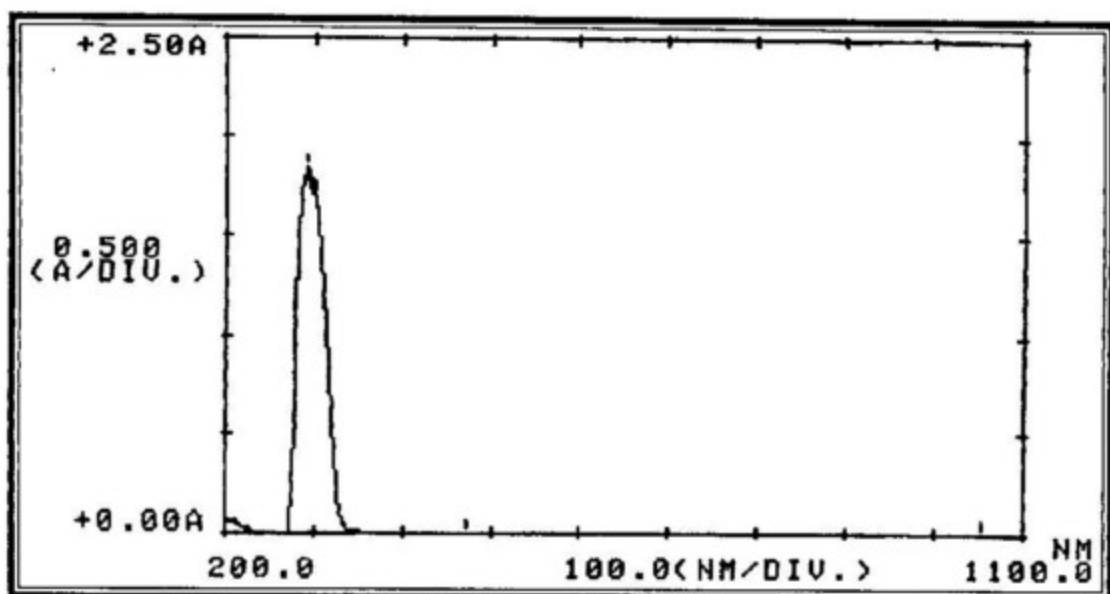


Fig.(6) U.V. spectrum of compound (13)

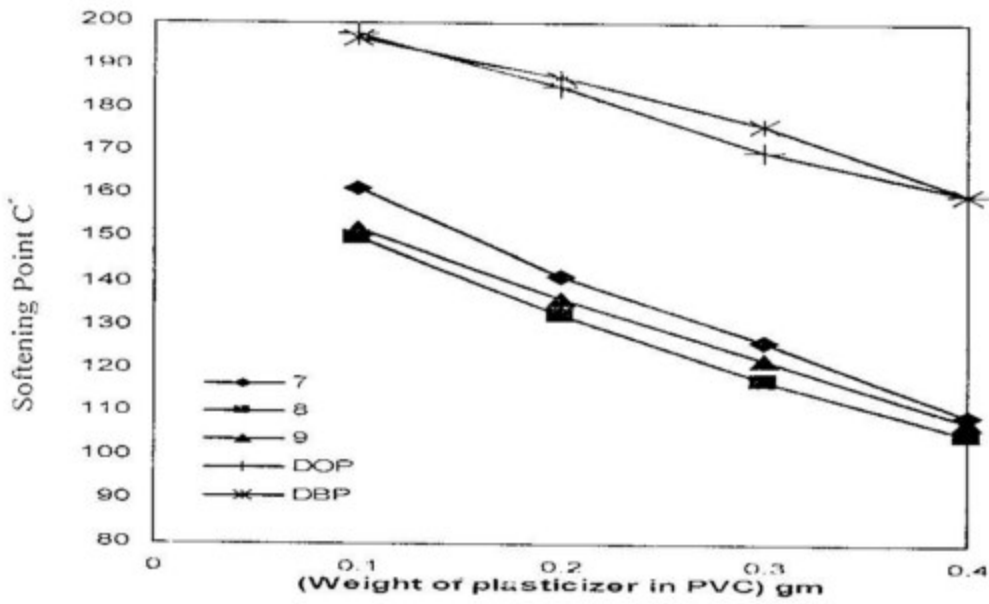


Fig.(7): Softening curve of methacrylate esters compared with (DOP) and (DBP)

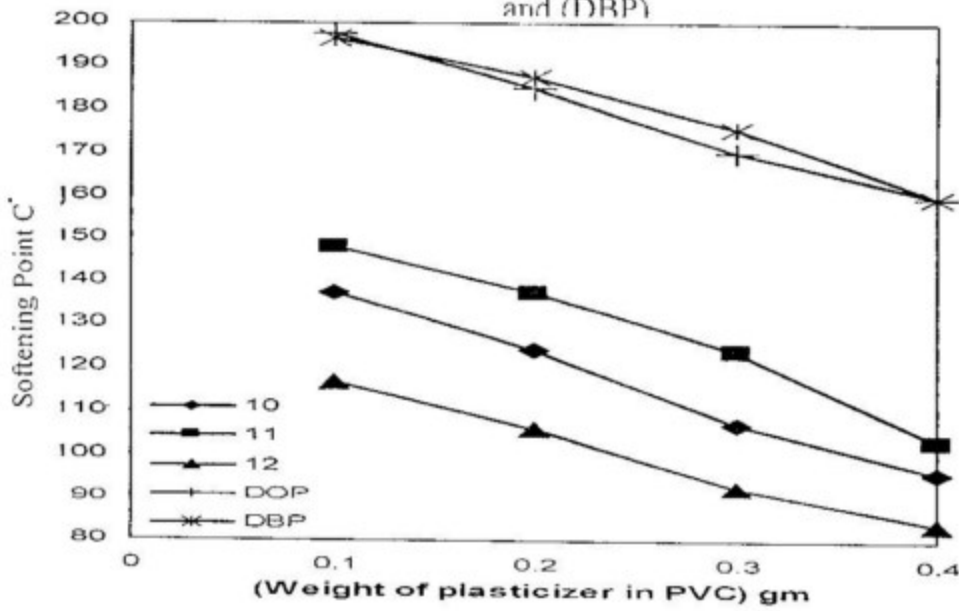


Fig.(8): Softening curve of benzoate esters compared with (DOP) and (DBP)

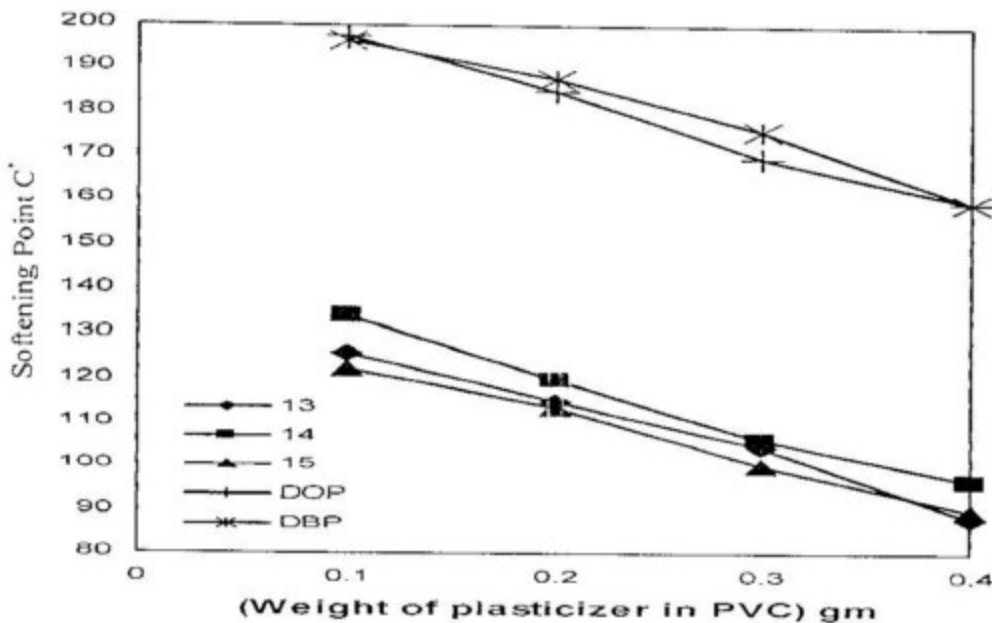


Fig.(9): Softening curve of cinnamate esters compared with (DOP) and (DBP)

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تحضير استرات N- معوض فثال ايميديل جديدة وتطبيقها كملدنات لبولي (كلوريد الفايثيل)

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الخلاصة

تضمن البحث تحضير ثلاثة من حوامض N-(هيدروكسي فنيل) فثال اميك بمنتوج عالي قدره (٩٢-٩٥)% وذلك من تفاعل مركبات اورثو، ميثا وبارا امينوفينول مع انهيدريد الفثاليك.

ثم سحب الماء والغلق الحلقي لحوامض الفثال اميك المحضرة باتباع تقنية الصهر وبذلك تم تحويلها الى مركبات N-(هيدروكسي فنيل) فثال ايميدات المقابلة وبمنتوج عالي قدره (٨٦-٩٠)% ثم تم تحويل الفثال ايميدات المحضرة الى استرات الميث اكريلات، البنزوات والسينامات المقابلة وذلك من خلال معاملتها مع كلوريدات حوامض مختلفة بوجود ثلاثي اثيل امين.

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 تلدن PVC وقد تم ذلك من خلال اعداد ستة وثلاثون نموذج من PVC مع الاسترات المحضرة وفق نسب وزنية معينة ثم سجلت درجات التلدن لجميع هذه النماذج. لقد اوضحت النتائج بان اضافة الاسترات المحضرة الى PVC تحدث انخفاضاً واضحاً في درجة تلدن البولييمر ويزداد الانخفاض مع زيادة تركيز الاستر (الملدن) في النموذج.

اما لغرض التعرف على كفاءة التلدن 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 تلدن PVC.