Modification of Poly[Styrene-Co-Butadiene] Rubber to Polymers Containing Pendant Amic Acid; Isoimide and Imide Isomerization of the Polymer Containing Isoimide to the Corresponding Imide

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Abstract

During this resceach, some chemical modifications have been done on poly[styrene-butadiene] rubber. Obviously, chemical modified polymers have new different chemical and physical properties with expected new applications.

The first chemical modification done are introduce of ($-NO_2$) group into poly[styrene-butadiene], then reduction of this group to ($-NH_2$) using $S/Na_2S.xH_2O$ to obtain poly[(p-aminostyrene)-butadiene]. When primary amine group allowed to react with anhydrous phthalic acid we obtained the polymer which contain amic acids, then last polymer was dehydrated using strong dehydrating agents, N,N-dicyclohexylcarbodimide (DCC), and trifloroacetic anhydride-triethylamine, we obtained polymer contain pending isoimide, then the isomerization using heat and acid or base, but we found that the polymer was resist to rearrange to corresponding imide, and when the amic acid polymer was allowed to react with a mixture of sodium acetate – acetic anhydride we obtained imide with good yield. Structures of all prepared polymers were confirmed by the measurement of softing points, viscosity, solubility in different solvents, FTIR, UV, H-NMR spectroscopy, thermalstability study using thermogravimetry analysis technique TGA, and some specific tests.

Introduction

Although the poly[styrene-butadiene] elastomer was originally manufactured during the war years as a rather mediocre replacement for natural rubber, which was unavailable. A major reason for their populatory is cost. Quality, however is also important since present day, styrene-butadiene rubbers (SBR) also have better abration characterstics and better cut-growth resistance than natural rubber. With their lower unsaturation SBR, also have a better heat resistance and better heat-agine qualitys, SBR extrution and smoother and maintain their form better than natural rubber dose[1].

Although of the high used of SBR, however the addition of imide or isoimide group increase the employment of the polymer in other fields.

Polyimides are a very interesting group of incredibly strong astoundingly heat and chemical resistant, and excellent mechanical properties. During the past two decades the demand for polymers suitable for use as high as 371°C and or able to withstand high temperature as long as 60.000 hours has a demand particulary in the aerospace industry[2-3].

Polyisoimides are important industrial polymers because of their improved solubility and curing properties. Polyisoimide are also of fundamental importance because they are multifunctional group polymers in which two type of chemical reactions, an isoimid-imide, isomerization and cross linking reaction occur in one

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system. Thus with increased cure time both reactions cause the system to became more rigid[4].

For this reasons mentioned earlier we report the synthesis of new polymers contains pendant imides, and isoimides for the first time.

Experimental

Nitration of poly[styrene-Co-butadiene] Rubber[5]

In a 500 ml three necked round bottom flask fitted with a dropping funnel and reflux condenser protected with calcium chloride tube, 24 ml of fuming nitric acid were placed, then 30 ml of glacial acetic acid were added in portions with shaking. The mixture was kept cool during addition by immersing the flask in cold water. The funnel was loaded with a solution of 3 gm poly[styrene–butadiene] Rubber dissolved in 60 ml of chloroform. The flask was surrounded with ice and cooled before addition of poly[styrene–butadiene] solution. The addition was performed dropwise with stirring. The mixture was refluxed for three hours at (50-60)°C and added gradually to excess cold water with stirring. The precipitated polymer was filtered and purified by dissolving in dioxane and reprecipitated in cold water.

Physical properties of the dry product poly[p-nitrostyrene-butadiene] are listed in tables (I-V). FTIR spectrum showed the following major absorption :

3080cm^{-1} $\nu_{=C-H}$ olefinic; 3060 cm^{-1} $\nu_{=C-H}$ aromatic; 2956 cm^{-1} ν_{C-H} alkane; 1630 cm^{-1} $\nu_{C=C}$ olefinic; 1556 cm^{-1} ν asym; 1346 cm^{-1} ν sym; 856 cm^{-1} ν_{C-N} aromatic and para substituted.

Preparation of poly[p-(aminostyrene)-butadiene][6]

In a 250 ml two-necked round bottom flask fitted with adropping funnel and a reflux condenser, 1.6 gm of Beta-sulfur and 4 gm of anhydrous sodium sulfide were dissolved in 30 ml dioxane. The mixture was heated on a hot plate for (15-20) min. with occasional stirring. The funnel was loaded with a solution of 4 gm poly[p-nitrostyrene-butadiene] dissolved in 60ml of dioxane. The latter solution was added dropwise with stirring. The mixture was refluxed for additional three hours resulting in a clear deep orange solution. The mixture was left for five hours, a deep red solution contains a yellow precipitate formed, the precipitate was filtered on Buchner funnel added gradually to 500 ml cold distilled water and netralized with 25% sodium hydroxide, which caused precipitation of the polymer. The separated polymer was filtered, washed with distilled water purified by carbon disulfide and dried at 50°C. The physical properties of the product poly[p-aminostyrene-butadiene] are listed in table (I-V). FTIR spectrum are showed the following major absorptions:

(3423-3286)cm^{-1} ν_{N-H} ; 3075cm^{-1} ν_{C-H} aromatic ; 3062 cm^{-1} ν_{C-H} olefinic; 2927 cm^{-1} ν_{C-H} alkane ; 1628 cm^{-1} $\nu_{C=C}$ olefinic, 873 cm^{-1} ν out of the plane aromatic para substituted.

Preparation of poly [N-(p-styrene-butadiene) phthalamic acid][7]

In a 250 ml round bottom flask 1.48 gm (0.01mole) of phthalic anhydride was dissolved in 20 ml of dry benzene to this solution was added a solution of (0.01mole) of poly[p-aminostyrene-butadiene] in 50 ml of dry benzene. The resulting mixture was stirred at (50-60) °C for 6 hrs, petroleum ether was added to produced precipitate, and washed in acetone for purification. The physical properties of the product poly[N-(p-styrene-butadiene) phthalamic acid] are listed in tables (I-V). FTIR spectrum showed the following major absorption:

(3400-2750)cm^{-1} broad ν_{N-H} and , $\nu_{=C-H}$ olefinic; 1726cm^{-1} $\nu_{C=O}$ of ; 1705cm^{-1} $\nu_{C=O}$ amide; 1638 cm^{-1} $\nu_{C=C}$

olefinic; 875cm^{-1} out of the plane aromatic para substituted.

Preparation of poly[p-(phthalisoimidyl) styrene-butadiene] rubber

Two literature procedures were used here with few modifications[8-9]:

Trifluoroacetic Anhydride (TFAA) and Triethylamine (TEA).

Mixture of (0.02mole) of poly[N-(p-styrene-butadiene) phathalamic acid], (0.02 mole) of (TEA) in 50 ml DMSO or DMF was refluxed for 25 min. and then cooled with an ice-salt bath to -5°C, while (TFAA) was added dropwise with stirring for 1 hr. The reaction mixture was left at room temperature for over night, then triethylamine hydrochloride was filtered. When the filtrate was added to ice distilled water, a precipitate was formed which then filtered off, and purified by dissolving in dilute sodium bicarbonate solution, and poly[p-(phthalisoimidyl) styrene-butadiene] was collected as white yellow precipitate.

N,N`-dicyclohexylcarbodiimide (DCC)

In a round bottom flask (0.02 mole) of the previously prepared poly[N-(p-styrene-butadiene) phthalamic acid], was dissolved in 50 ml of DMSO or DMF. To this solution was added a solution of (0.02 mole) DCC dissolved in 20 ml of DMSO or DMF at at 0°C using an ice bath. The addition was continued for a period of 2 hrs with stirring, the reaction was stirred for over night at room temperature and the precipitated N,N`-dicyclohexyl urea (DCU) was filtered off. The solution was left for 8 hrs to give further precipitate of (DCU), then filtered off again. The solution was evaporated under reduced, pressure and a white precipitate of poly[p-(phthalisoimidyl)styrene-butadiene] was separated out. The product was washed with dilute sodium bicarbonate extracted with THF and reprecipitated with petroleum ether b.p (30-40)°C. The white precipitate filtered and dried under vacume. Physical properties of the precipitates poly[p-(phthalisoimidyl)styrene-butadiene] are listed in tables (I-V). FTIR spectrum showed the following major absorptions:

(3099-3059) cm^{-1} ν_{C-H} aromatic and $\nu_{=C-H}$ olefinic; 2955 cm^{-1} ν_{C-H} alkane; 1733 cm^{-1} $\nu_{C=O}$ lacton; 1642 cm^{-1} $\nu_{C=N}$; 1622 cm^{-1} $\nu_{C=C}$ olefinic.

Preparation of poly[p-(phthalimidyl)styrene-butadiene][7]

In a round bottom flask (0.02 mole) of poly[N-(p-styrene-butadiene) phthalamic acid] was dissolved in 30 ml of dry DMSO or DMF. To this solution was added a mixture of one equivalent of anhydrous sodium acetate and excess acetic anhydride from a dropping funnel dropwise during 35 min with stirring. Stirring was continued for 3 hrs. Then the mixture was added to a beaker containing ice water and a precipitate was formed which the filtered and purified by dissolving in dilute sodium bicarbonate solution. Physical properties of the newly prepared poly[p-(phthalimidyl)styrene-butadiene] are listed in tables (I-V). FTIR spectrum showed the following major absorptions:

(3090-3054) cm^{-1} ν_{C-H} aromatic and $\nu_{=C-H}$ olefinic ; 2953 cm^{-1} ν_{C-H} alkane ; 1780 cm^{-1} $\nu_{C=O}$ asym-imide (shoulder); 1692 cm^{-1} $\nu_{C=O}$ sym-imide; 1623 cm^{-1} $\nu_{C=C}$ olefinic ; 1392 cm^{-1} ν_{C-N}.

Isomeriztion of poly[p-(phthalisoimidyl) styrene-butadiene] rubber

A- Thermally according to literature method[10].

B- Using sodium acetate – heating[8].

C- Hydrolysis in acid medium[11].

The stability of the compound poly[p-(phthalisoimidyl)styrene-butadiene] it was found that it was

resistant to isomerization thus, softening point and FTIR spectra of product was unchanged.

Results and Discussion

Ploy[p-(nitrostyrene)-butadiene] was prepared using fumed nitric and glacial acetic acid as a catalyst, according to the following equation[5].

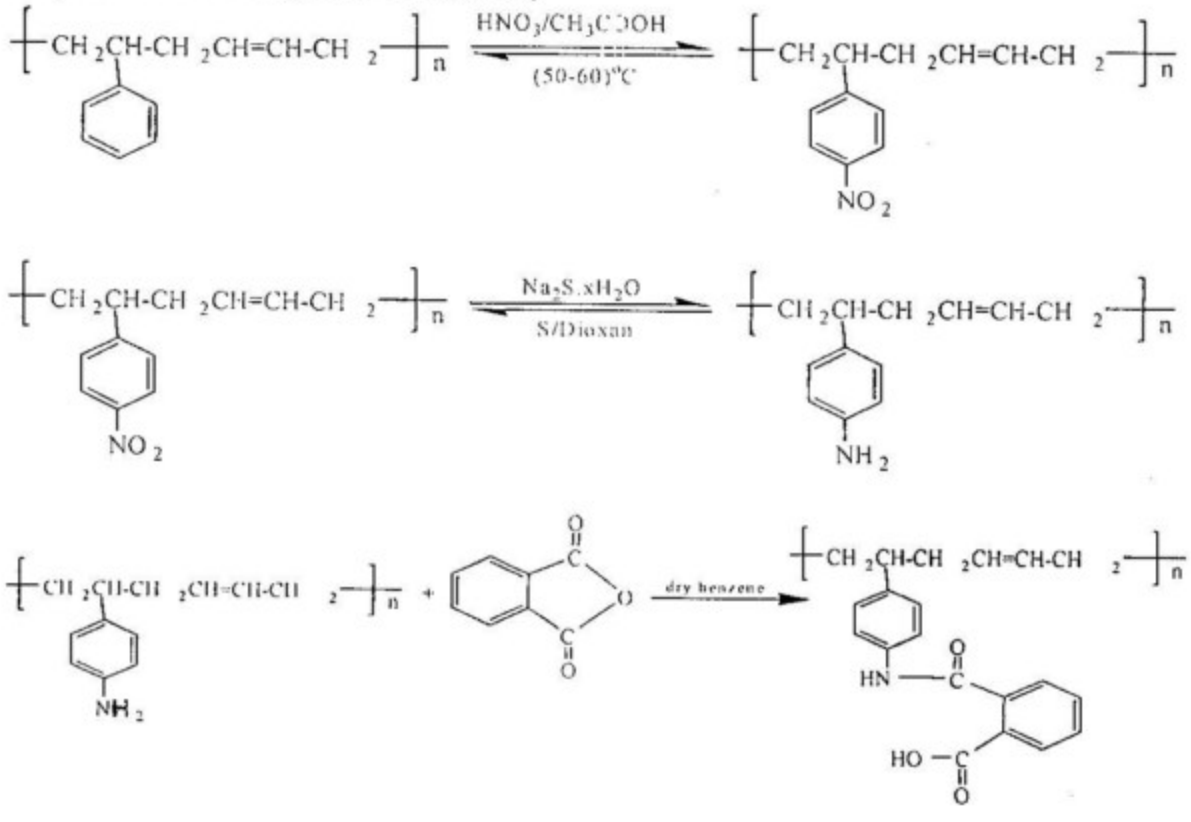
The reaction must be carried out in dry condition and low temperature because the rate limiting step contain a water molecule as a by product and oxidizing action of nitric acid. Also using glacial acetic acid instead of concentrated sulfuric acid in order to preserve the double bond[12].

FTIR spectra of this polymer showed the presence of ν asym at 1556 cm^{-1} ; ν sym at 1346 cm^{-1} and the $\nu_{C=C}$ olefins at 1630 cm^{-1}, also the presence of nitrogen of $-NO_2$ group which was introduced on the polymer was confirmed by using sodium fusion test.

Reduction of $-NO_2$ group in poly[p-(nitrostyrene-butadiene] was not successful by using Fe/HCl or with other metals such as Zinc or Tin. However the use of anhydrous sodium bisulfide which is considered as a selective reducer in the presence of sulfur in dioxane solvent[6].

FTIR spectrum of the poly[p-(aminostyrene)-butadiene] showed amino group intense doublet band at (3423-3286) cm^{-1} and disappearance of the absorption of nitro group.

Polymer with pending phthalamic acid was prepared according to the literature[7]. The equation of the reaction is as follow:

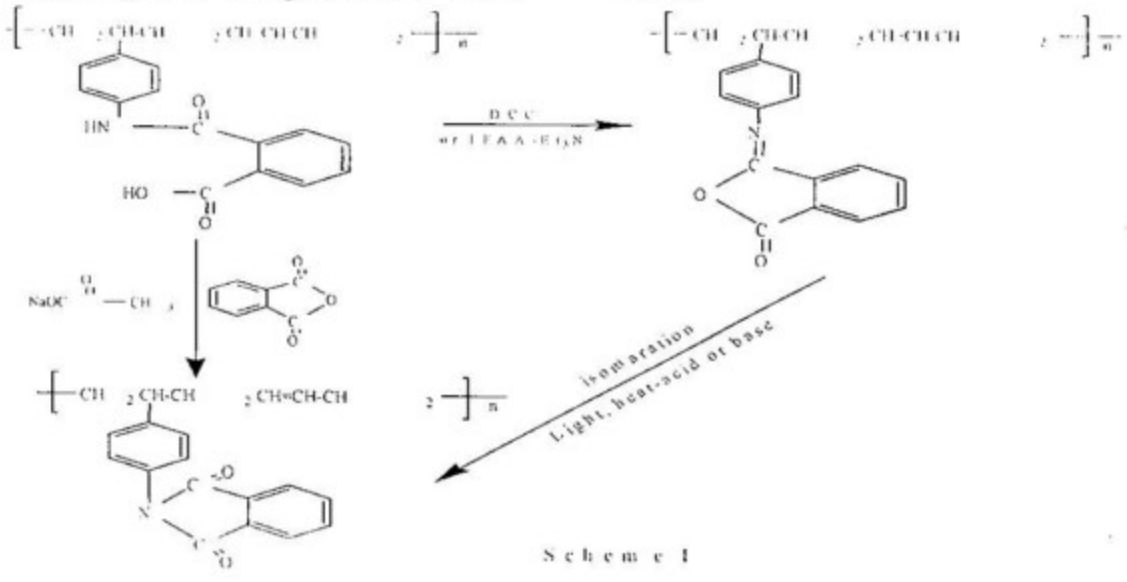


FTIR spectrum of amic acid polymer show broad band for NH, ν_{N-H} at (3400-2750) cm^{-1} overlapping with OH of ν_{COOH}.

When the amic acid polymer was react with DCC or TFAA-Et_3N we obtained isoimide as a product due to with drawing a water molecule. It was found that the dehydration using DCC was better than the used of TFAA-Et_3N as it was show from the yield and purity.

FTIR spectrum shown of the prepared isomide polymer showed absorption of –C=N at 1642 cm^{-1}; isoimide carbonyl (Lacton) at 1733cm^{-1} And absence of OH and NH absorption.

It was found that the prepared isoimide polymer resist isomerization by heat, light or using acidic or basic solution. FTIR spectrum of phthalimide polymer show asym imide (Shoulder) carbonyl absorption at 1780 cm^{-1} and sym-imide (Sharp) at 1692 cm^{-1}, disappearance of –OH (carboxylic) and NH absorption. Scheme 1 shows the performed reactions and transformation, isoimide-imide.



Scheme 1

Structures of all prepared polymers were confirmed by the measurement of softening point, intrinsic viscosity [η_{int}], and %conversion as it shown in table (I), solubility in different solvents as shown in table (II), UV and H-NMR spectroscopy as it shown in tables (III-IV), and thermal stability study using thermogravimetry analysis technique TGA, and several parameters were calculated from the thermogram curves such as activation energy for the decomposition the temperatures in which 10% and 50% of polymers are decomposed[13], Table (V) show this parameters.

It is well known that polyimides are stable and resist to heat and pressure, since they loss only 4.2% from their weight when they are heated to 440°C, furthermore they have high activation energy.

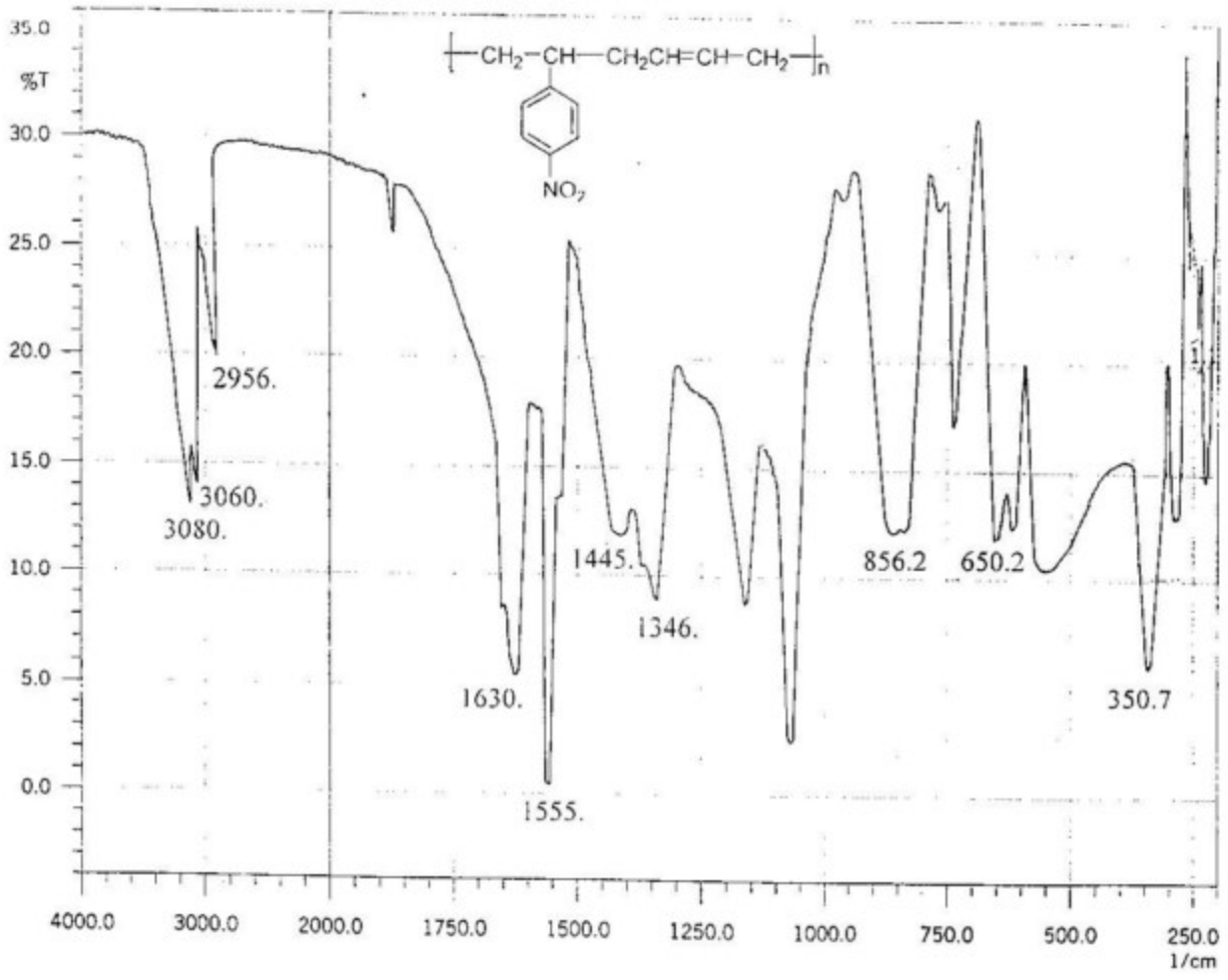


Fig (1): FTIR spectra for poly[(p-nitrostyrene)-butadie

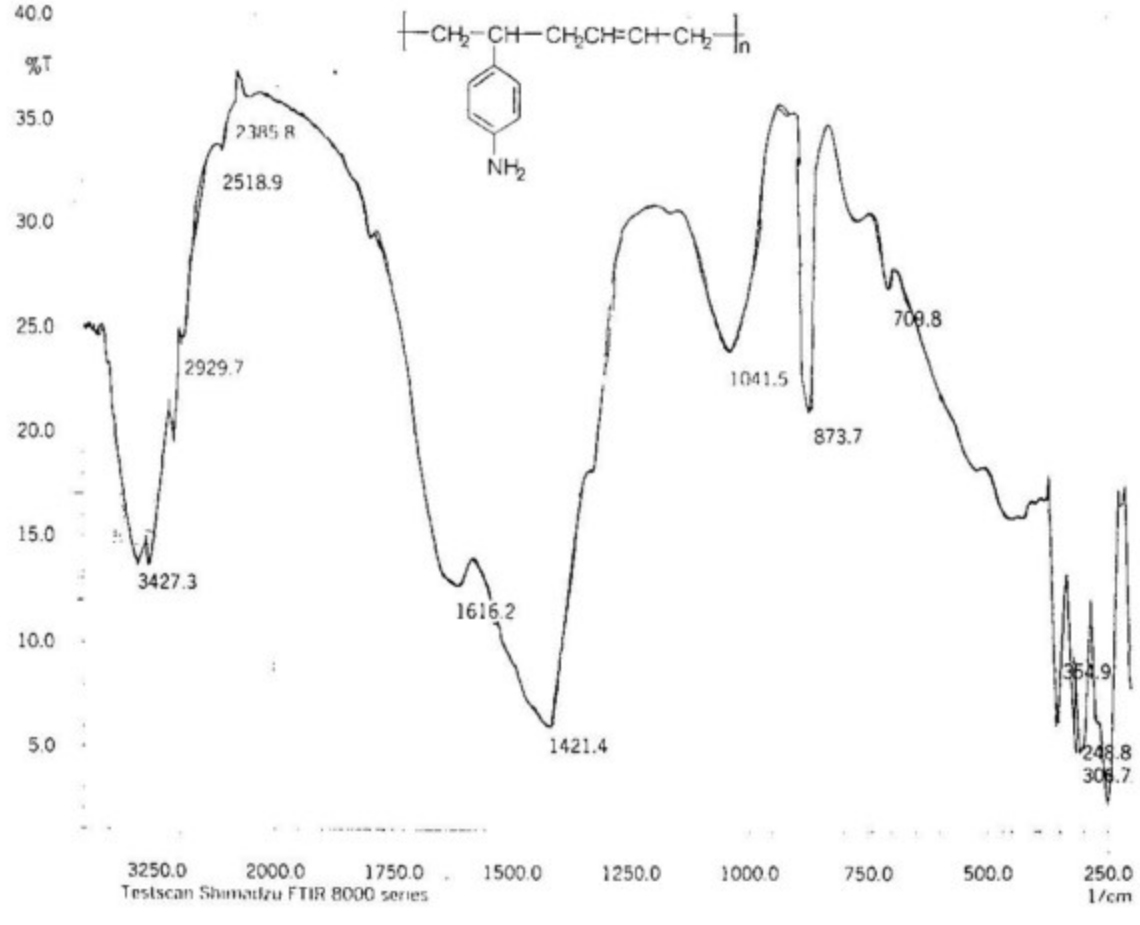


Fig (2): FTIR spectra for poly[(p-aminostyrene)-butadiene]

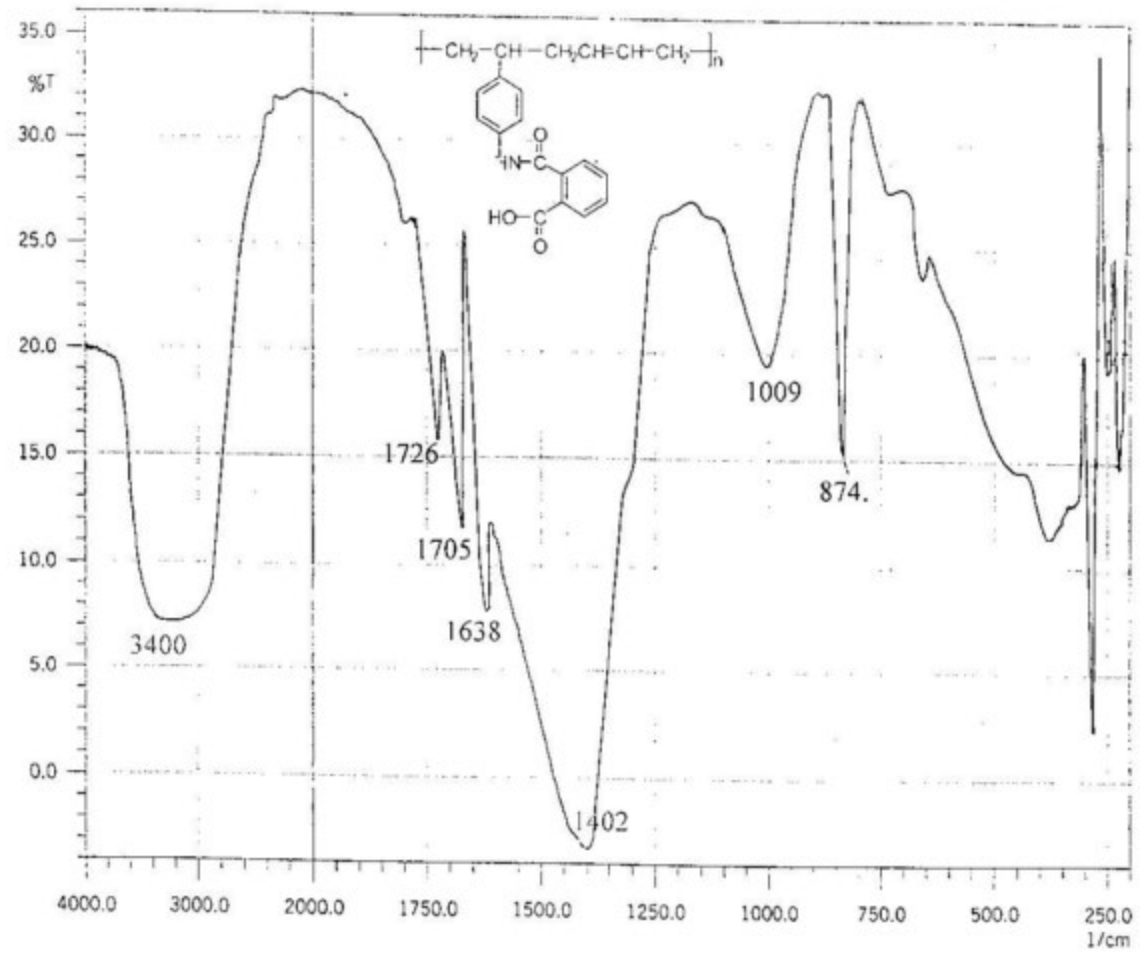


Fig (3): FTIR spectra for poly[N-(p-styrene-butadiene)phthalamic acid]

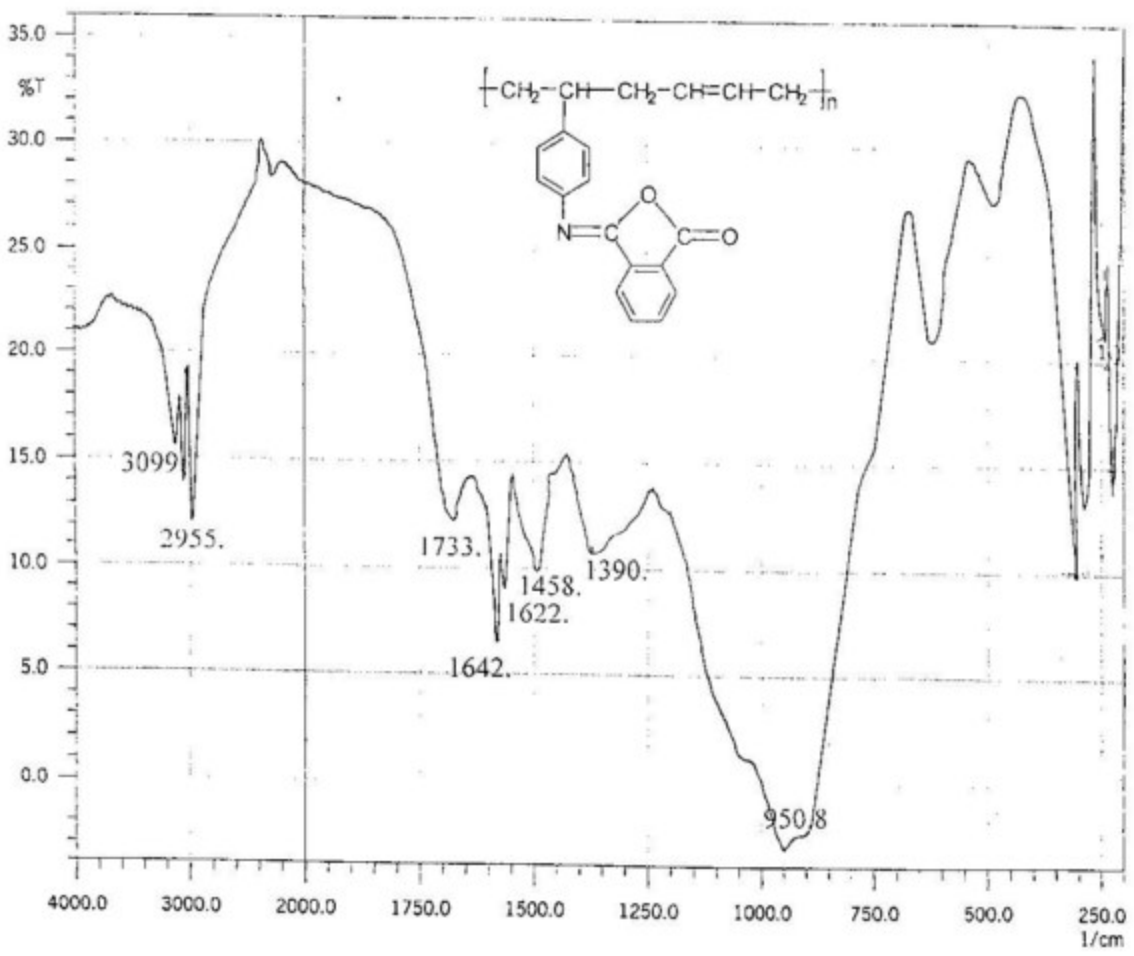


Fig (4): FTIR spectra for poly[p-(phthalisoimidyl)styrene-butadiene]

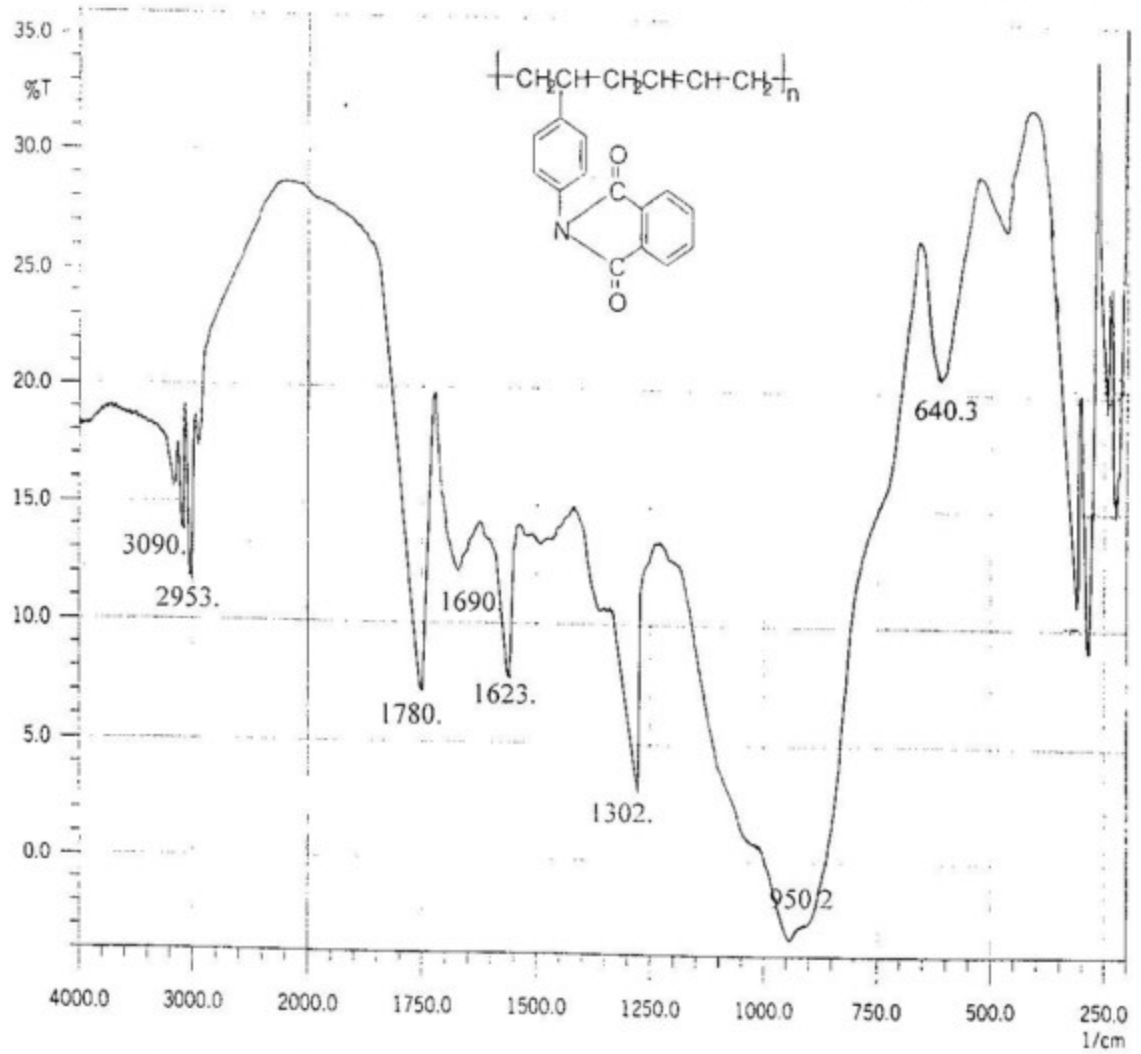


Fig (5): FTIR spectra for poly[p-(phthalimidyl)styrene-butadiene]

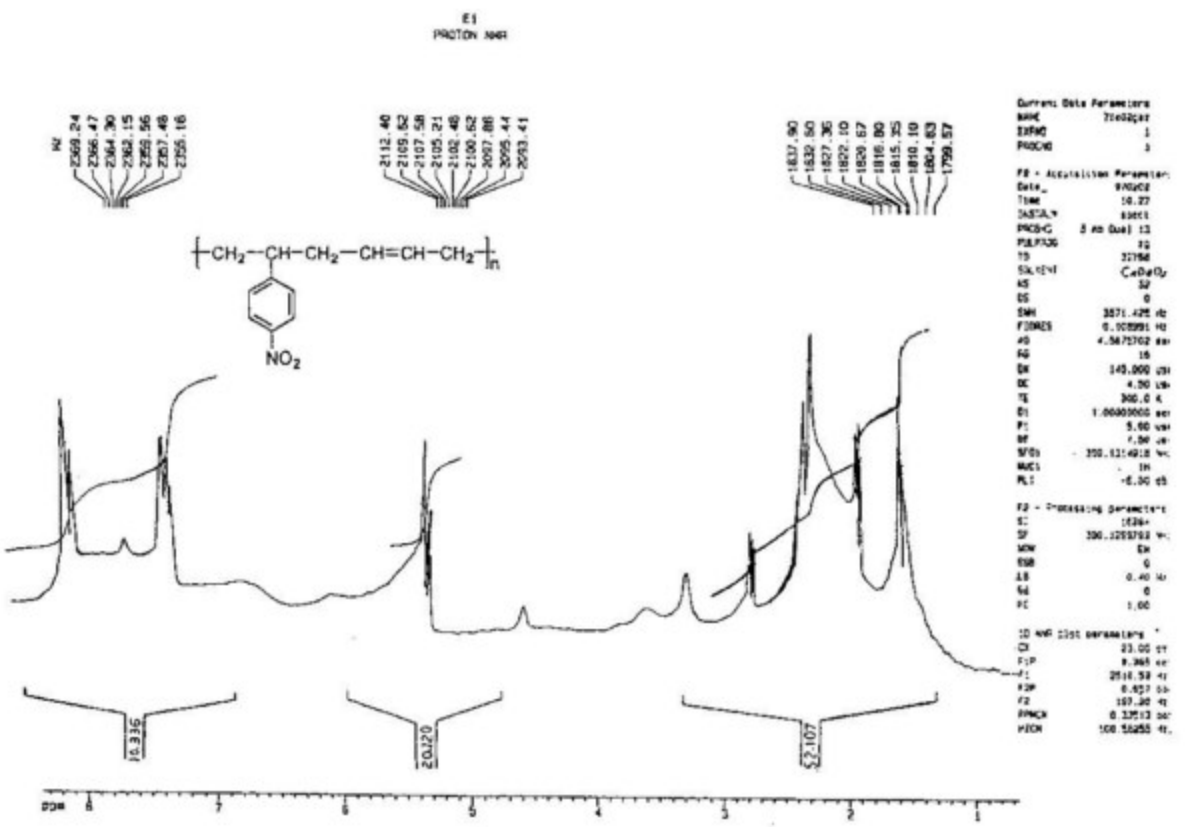


Fig (6): NMR spectrum for poly[(p-nitrostyrene)-butadiene

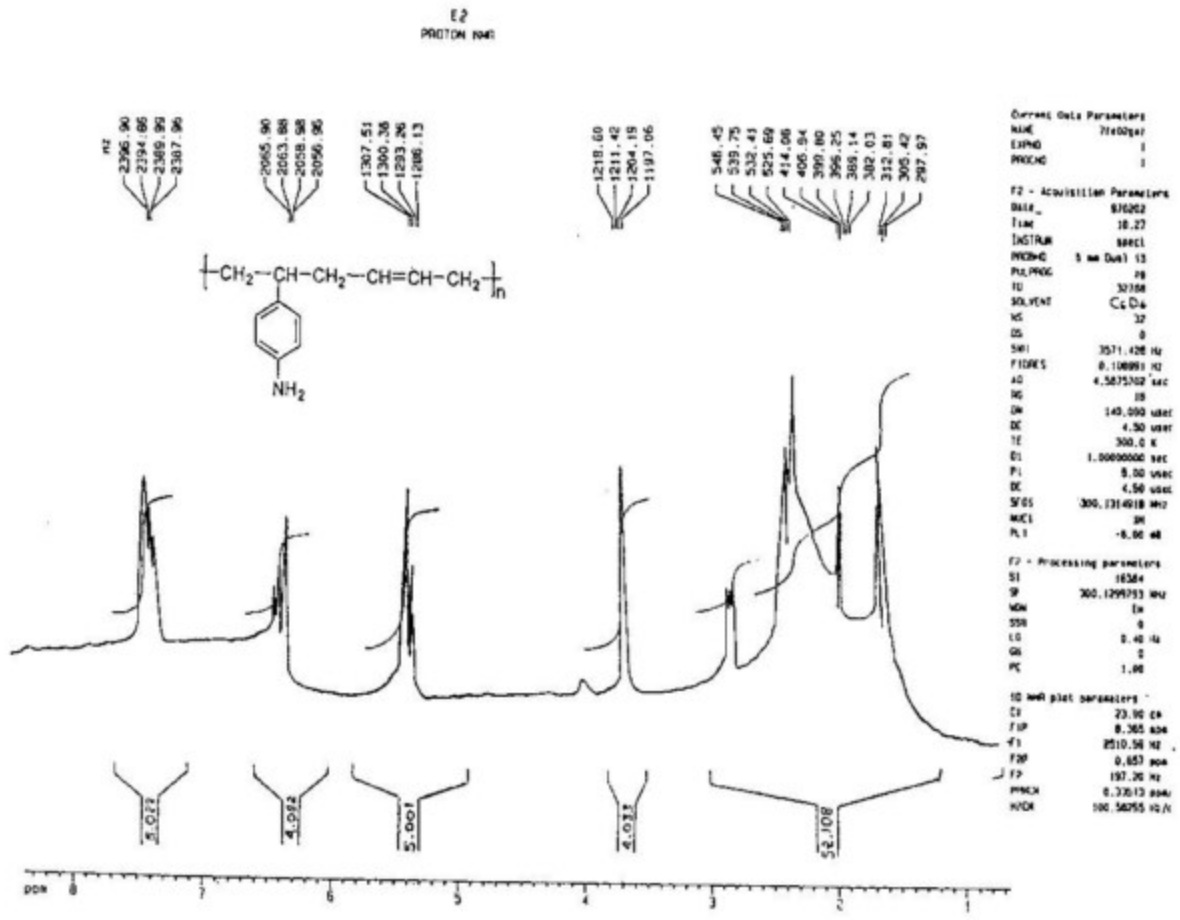


Fig (7): NMR spectrum for poly[(p-aminostyrene)-

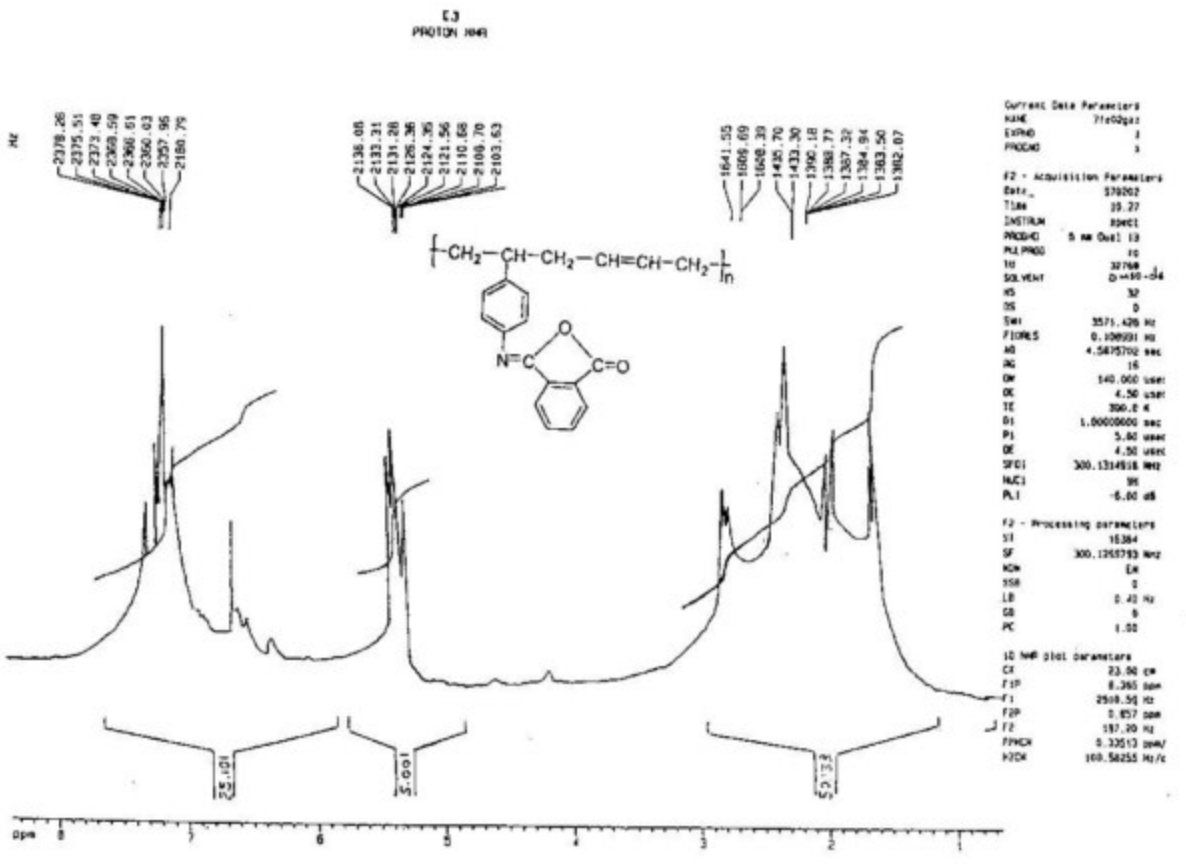


Fig (8): NMR spectrum for poly[p-(phthalisoimidyl)styrene-

Table (2) Solubilities of the prepared polymers

name	water	ethanol	Benzen or Toluene	dioxa u	DC M	DC E	$CHCl_3$ or CCl_4	TH F	DM F	DMS O	PE S
Poly[(p-nitrostyrene)-butadiene]	PS H	PSH	In	S	In	In	In	In	S	S	In
Poly[(p-aminostyrene)-butadiene]	In	In	S	In	PS H	PS H	PSH	PS H	S	PS	In
Poly[N-(p-styrene-butadiene)phtha; amic acid]	In	In	PSH	In	PS H	PS H	PSH	PS H	S	S	In
Poly[P-(phthalisoimidyl) styrene-butadiene]	In	In	In	In	In	In	In	In	PS	S	In
Poly[P-(phthalisoimidyl) styrene-butadiene]	In	In	In	In	In	In	In	In	S	PS	In

Abbreviation:- (S):soluble, In=insoluble, PS=Partial soluble, PSH=Partial soluble hot
DCM:dichloromethane, DCE=dichloroethane, PES=petroleum ether spirit.

Table (3) Ultra violet spectra of the poly[styrene-butadiene]derivatives.

Name	λ_{1max} (nm)	A_1	E_1KCal/mole	λ_{2max} (nm)	A_2	E_1KCal/mole
Poly[styrene-butadiene]	275.0	1.115	104.00	249.0	1.338	114.86
Poly[(p-nitrostyrene)-butadiene]	278.0	1.800	102.88			
Poly[(p-aminostyrene)-butadiene]	284.0	1.238	100.70	310.0	1.222	92.25
Poly[N(p-styrenebutadiene)phthalamicacid]	282.0	0.851	101.42			
Poly [P(phthalisoimidyl)styrene-butadiene]	276.0	0.917	103.62			
Poly[P(phthalimidyl)styrene-butadiene]	270.0	0.491	105.93			

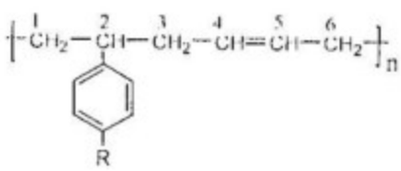


Table (4) H-NMR(P.P.M.), of the poly[styrene-butadiene] Rubber derivatives

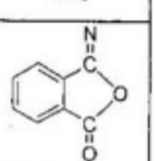
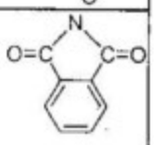
Name	$\delta(H2)^1$	$\delta(H)^2$	$\delta(H)^3$	$\delta(H)^4$	$\delta(H)^5$	$\delta(H)^6$	δH Aromatic	δH -R	R
Poly[(p-nitrostyrene)-butadiene]	1.62 (d,2H)	2.85 (p,1H)	2.30 (t,2H)	5.45 (q,1H)	5.45 (m,1H)	1.95 (d,2H)	7.45-8.3 (m,m,4H)		$-NO_2$
Poly[(p-aminostyrene)-butadiene]	1.62 (d,2H)	2.85 (p,1H)	2.30 (t,2H)	5.45 (q,1H)	5.45 (m,1H)	1.95 (d,2H)	6.5-7.4 (m,m,4H)	3.7 (S,2H)	$-NH_2$
Poly[(p-phthalisoi-midyl) styrene-butadiene]	1.62 (d,2H)	2.83 (p,1H)	2.28 (t,2H)	5.45 (q,1H)	5.45 (m,1H)	2.0 (d,2H)	6.5-7.5 (m,4H)	(7.7,7.9) (m,4H)	
Poly[(p-phthalim-idyl) styrene)-butadiene]	1.6 (d,2H)	2.81 (p,1H)	2.30 (t,2H)	5.43 (q,1H)	5.40 (m,1H)	2.0 (d,2H)	6.5-7.6 (m,4H)	(7.9-8.1) (m,4H)	

Table (5) Data obtained from TG and DTG of the poly[styrene-butaiene] derivative.

Name	Sample weight (mg)	10%wt loss Temp C	50%wt loss Temp C	Peak 1 Temp C	Peak 2 Temp C	Peak 3 Temp C	Activation energy ΔE Cal/mole	Temp. Range C
Poly[styrene-butadiene]	30	376	481	406 16%wt loss			12.826	320-402
Poly[(p-nitrostyrene)-butadiene]	2.581 69	128	355	200 22.4% wt loss	340.7 47% wt loss	529 82.7% wt loss	6.336	256-300
Poly[(p-aminostyrene)-butadiene]	1.761 77	358	>700	134 5.7% wt loss	378.7 14%wt loss	688 38.6% wt loss	22.846	548-612
Poly[N-(p-styrene-butadiene) phthalamic acid]	2.947 55	326	>700	82.2 4.3% wt loss	381 15.3% wt loss	463 24.4% wt loss	8.399	336-480
Poly [P(phthalisoimidyl)styrene-butadiene]	2.765 09	500	>>700	40.8 2.4% wt loss	311.6 8.1% wt loss	522.9 15.3% wt loss		
Poly[P(phthalimidyl)styrene-butadiene]	2.765 09	688	>>700	116.3 2.4% wt loss	332.3 5.6% wt loss	449.1 4.2% wt loss		

Reference

1- Pyriadi, T.M., G.A.Adam **(1989).** In "Contermporary polymer chemistry" 1st Ed. University of Mousel press. In Arabic.

2- Fryd, M. **(1984).** In "Polyimides: Synthesis, characterization and properties" Vol. 1, Ed. Mittal. K.L., Plenum New York.

3- Takekoshi, T., **(1996).** In "Polyimides : Fundamentals and applications" chapter 2 Edts. Ghosh. M.K. and Mittal, K.L. Marcel, New York.

4- Huang, Wei Xin, **(1995).** Study of Acetylene-terminated polyisoimide and precursors by fourier transform infrared spectroscopy. DAI-B 55/12, p.5363.

5- Heniy, F. Ed **(1970).** In "The chemistry of the nitro and nitroso group" part 2. International publishers a division of John Wiley and Sons. New York. London. Sydney. Toronto.

6- Vogel A.I., **(1974).** In "A text book of practical organic chemistry" 3 Ed. Longman group limited London.

7- Cava, M.P., A.A. Deana, K. Muth. And M.J. Mitchel **(1961).** N-phenylmaleimide. Org. Syn. 41: 93.

8- Cotter, R.J., C.K. Savers and J.M. whenlan. **(1961).** The synthesis of N-substituted isomaleimide. J. Org. Chem. 26: 10.

9- Kretov, A.E., N.E. Kul Chitskya and A.E. Malnev **(1961).** The synthesis of polyimides via

polyisoimide precursors, J. Gen. Chem. USSR. 31: 2415.

10- A-Asli, N.J., **(2000).** Ph.D. thesis, "Modification of poly[vinyl chloride] to polymers containing pendant amic acid, imide, and isoimide" college of science, University of Baghdad.

11- Connel, J.W. and Watson VA **(2001)** physically persistent stabilizers by functionalization of polymers 224 high performace polymers. 13(1):23-34.

12- Morrison, R.T., R.N. Boyd. **(1987).** In Organic chemistry 5th Ed. Allyn Ana Bacon, Inc. Boston. London. Sydeny. Toronto.

13- Pecsok, R.L., L.D. Shilde, T. Cairns I.G. Mcwilliam **(1976).** In "Modern Methods of chemical anakysis". 2th Ed. John Wiely and Sons. New York. Chicherter. Brisbance Tornto. Sinngapore.

تحوير مطاط [ستايرين-مشترك-بيوتاديين] الى بوليمرات حاوية على مجاميع اميك وايميدات وايسوايميدات متدلية. ترتب البوليمر الحاوي على مجاميع الايسوايمدات الى الايميد المقابل

ذنون محمد بيريادي* سعاد محمد حسين الماجدي*

* د./ قسم الكيمياء-كلية العلوم-جامعة بغداد

الخلاصة

تم خلال هذا البحث انجاز بعض التحويرات الكيميائية على بولي [ستايرين-بيوتاديين] للحصول على بوليمرات محورة جديدة ذات صفات كيميائية وفيزيائية ولها تطبيقات جديدة متوقعة.

ان اول هذه التحويرات الكيميائية التي انجزت هي ادخال مجموعة ($-NO_2$) على البولي [ستايرين-بيوتاداين] ومن ثم تم اختزال هذه المجموعة الى ($-NH_2$) باستخدام $S/Na_2S.xH_2O$ فحصلنا على بولي [(بارا-امينوستايرين)-بيوتاداين] وعند تفاعل مجموعة الامين الاولية في البوليمر مع حامض الفثاليك اللامائي تكون لدينا البوليمر الحاوي على حامض الاميك، وعند سحب جزيئة الماء منه بوليمر الاميك باستخدام العوامل الساحبة القوية، ثنائي سايكلوهكسيل كاربوثنائي الاميد (DCC) وثلاثي فلورو حامض الخليك اللامائي-ثلاثي اثيل امين، تم الحصول على الايسوايميد المتدلي بولي [بارا-(فثال ايسوايميديل) ستايرين-بيوتاداين].

وعند اجراء عملية الترتب لبوليمر الايسوايميد باستخدام الحرارة - الحامض او القاعدة لوحظ انه مقاوم للترتب الى الايميد المقابل وبعد معاملة بوليمر الاميك مع مزيج من خلات الصوديوم اللامائية-حامض الخليك اللامائي تكون لدينا الايميد بولي [بارا-(فثالئميديل) ستايرين-بيوتاداين] تم اثبات تراكيب جميع البوليمرات المحضرة بقياس درجات التلين، اللزوجة الجوهرية [η]، الذوبانية في المذيبات المختلفة، اطياف FTIR ، UV، H-NMR ودراسة التحليل الحراري الوزني TGA، وبعض الكشوفات النوعية.