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Highly arylated bis-cyclopentadienones in the synthesis of aromatic condensation monomers and polymers

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Abstract

A great variety of condensation monomers—highly arylated bis-cyclopentadienones—have been prepared by the reaction of bis(α-diketones) with two-fold molar amounts of diarylacetones. Reaction of these monomers with bis-acetylenes and *N,N'*-bis-maleimides under Diels-Alder reaction conditions led to the formation of highly arylated polyphenylenes and polyimides combining outstanding tractability with excellent thermal properties. Alternatively, these monomers were transformed into the corresponding highly arylated bis(phthalic anhydrides), bis(naphthalic anhydrides) and diamines, which were used for the preparation of organo-soluble polyimides, polynaphthylimides and polynaphthoylenebenzimidazoles.

Keywords: Cyclopentadienones; Highly arylated bis-cyclopentadienones; Diels-Alder reaction; Highly arylated polyphenylenes; Highly arylated polyimides; Highly arylated tetracarboxylic acid dianhydrides

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Contents

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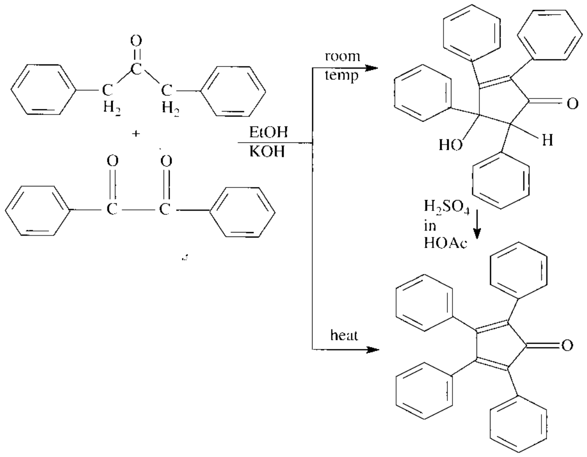
1. Introduction

Uses for aromatic polyimides [1], polynaphthoylenebenzimidazoles [2] and polyphenylenes [3] have been developed rapidly in recent years owing to their thermooxidative and thermomechanical properties. However, applications have been limited in many fields because these aromatic polymers are normally insoluble in common organic solvents [4]. Their excellent mechanical properties at high temperatures are due to the rigid structures which result in high glass transition temperatures or melting points. However the inter/intramolecular properties that lead to high glass transition temperatures and melting points often result in poor solubility. Modified structures with bulky aryl substituents have been synthesized that provide improved solubility [5–7]. The most effective synthetic method for the incorporation of multiple aryl substituents in aromatic monomers and polymers is based on the Diels-Alder reaction [8–10] using highly arylated bis-cyclopentadienones.

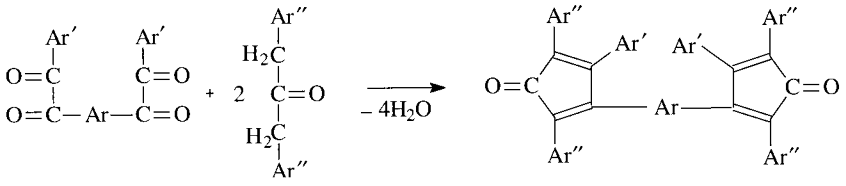
2. Synthesis and properties of bis-cyclopentadienones (bis-tetracyclones)

The most convenient method for the preparation of arylated mono-cyclopentadienone is the reaction between benzyl and 1,3-diphenylacetone [11]:



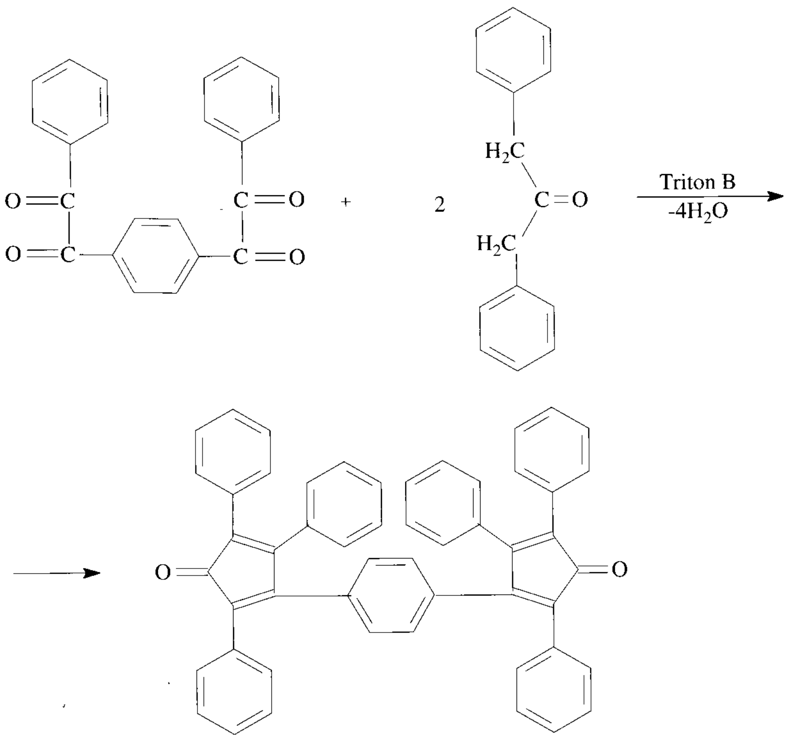
(1)

Similarly to the synthesis of mono-cyclopentadienones [11], arylated bis-cyclopentadienones (bis-tetraarylcyclones) were prepared using the base-catalyzed condensation of bis-benzyls [bis-α-diketones, bis(arylgloxalyl)arylenes] [12] with two-fold molar amounts of benzyl ketones (1,3-diarylacetones) in accordance with the scheme:



(2)

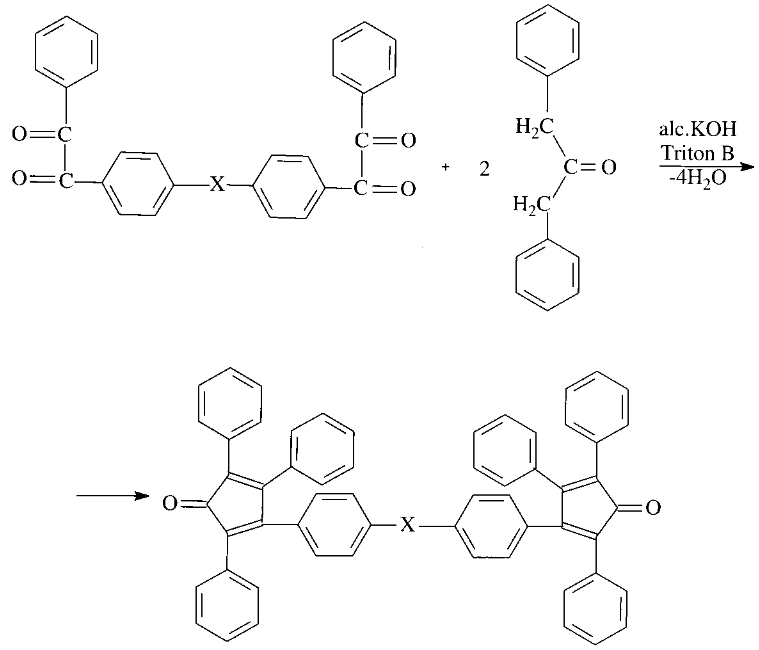
The simplest representative of bis-tetracyclones—1,4-bis(2,3,5-tetraphenylcyclopentadien-1-on-4-yl)benzene—was prepared by the reaction of 1,4-bis(phenylglyoxalyl)benzene with a two-fold molar amount of 1,3-diphenylacetone [13,14]:



(3)

Some properties of the target compound are given in Table 1.

Using base-catalyzed condensation of bi- and tri-nuclear bis(α-diketones) with two-fold molar amounts of 1,3-diphenylacetone [15]:

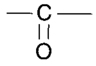


(4)

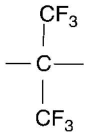
with —X— denoting:

$-(CH_2)_n-$; n = 3, 4, 6 [13]

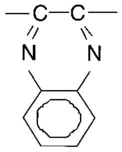
— —S— —O— $-(CH_2)-$ [16]



$-\underset{\underset{O}{\|}}{C}-$ [17] $-(CH_2)_n-$; n = 10, 14 [18]



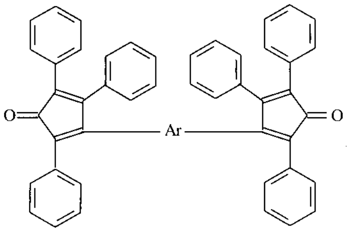
$-\underset{CF_3}{\overset{CF_3}{C}}-$ [19] —C≡C— [20]

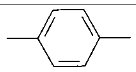
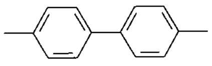
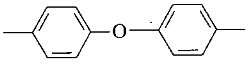
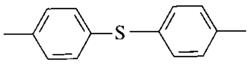
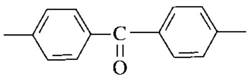
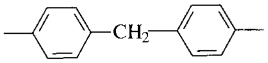
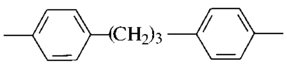
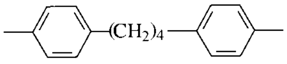
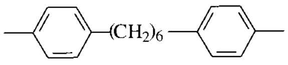
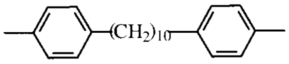
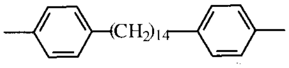
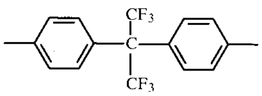
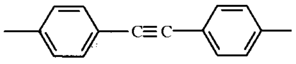
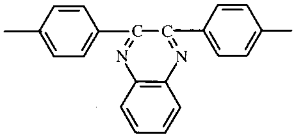


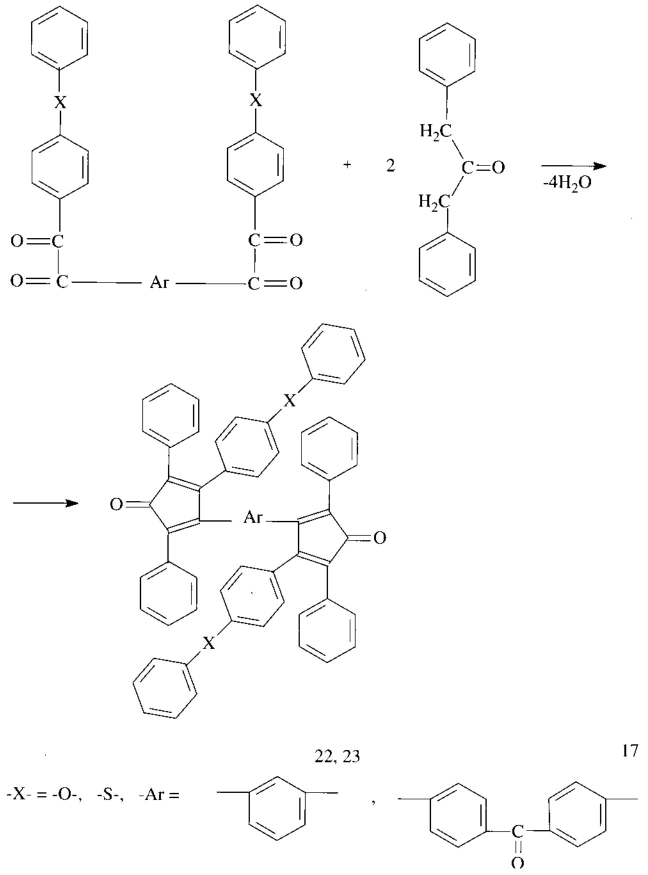
[21]

several phenylated bis-cyclopentadienones were obtained [13,16–21]; some properties of the target compounds are listed in Table 1. Along with bis-cyclopentadienones containing phenyl substituents several compounds containing additional groups—phenoxy [17,22,23], thiophenoxy [17,22,23], methyl [24,25] groups, and bromine [25] or fluorine [26] atoms—on phenyl side groups were prepared. Reaction of bis(α-diketone)s containing diphenyl ether and diphenyl sulfide terminal groups with two-fold molar amounts of 1,3-diphenylacetone led to the formation of bis-cyclopentadienones containing the above-mentioned bulky substituents [17,22,23]:

Table 1
Properties of phenylated bis-cyclopentadienones with the general formula



-Ar-	M.P.°C	Yield %	Ref.
	302-304	78 47	13 14
	293-294	89	16
	256-258	79	16
	277-279	53	16
	301	89	17
	248-249	40	16
	259-262	68	13 18
	234-235 252-253	18	13 18
	109-110 215-217	28	13 18
	158-160	41	18
	115-117	33	18
	236	94	19
	-	76	20
	325-326	92	17, 21



(5)

Some properties of the target bis-cyclopentadienones are given in Table 2.

Table 2
Properties of arylated bis-cyclopentadienones

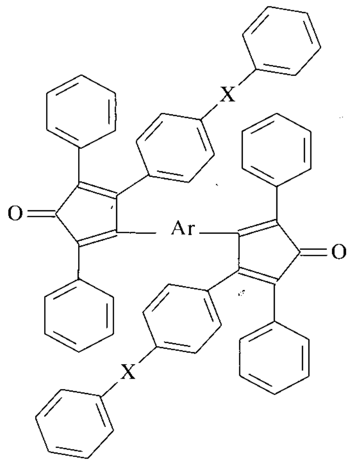
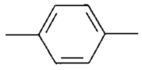
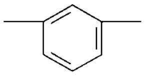
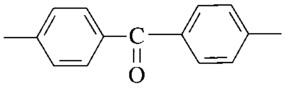
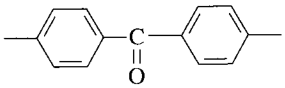
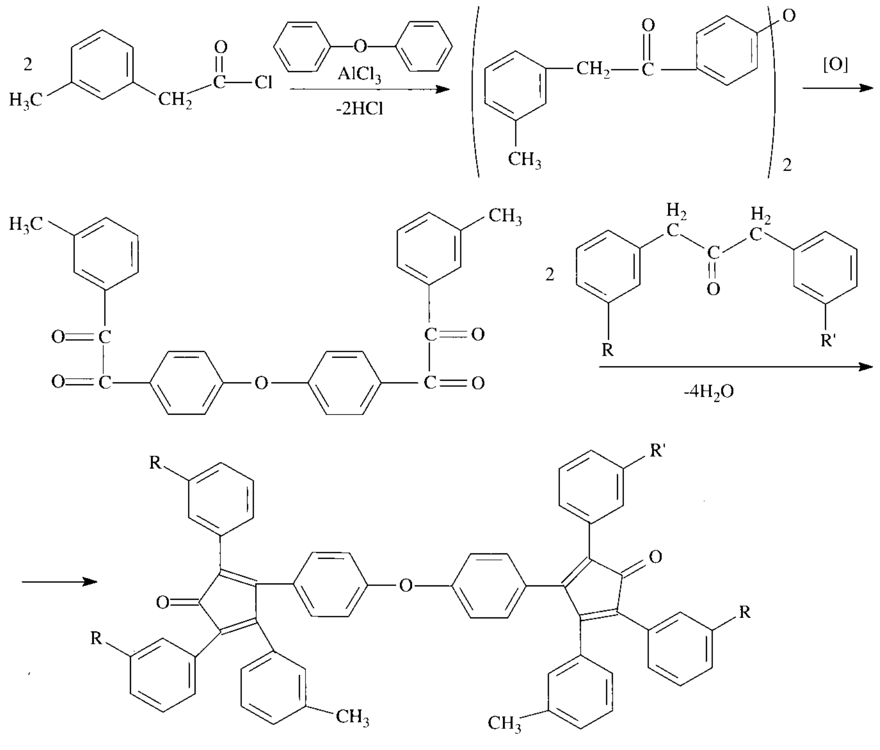


Table 2 (*continued*)

-Ar-	-X-	M.P. °C	Yield %	Ref.
	-O-	205-206	82.7	23
	-S-	202-203	98.2	23
	-O-	450	88.4	17
	-S-	450	84.5	17

Bis-cyclopentadienones containing methyl substituents have been prepared according to the scheme [24,25]:



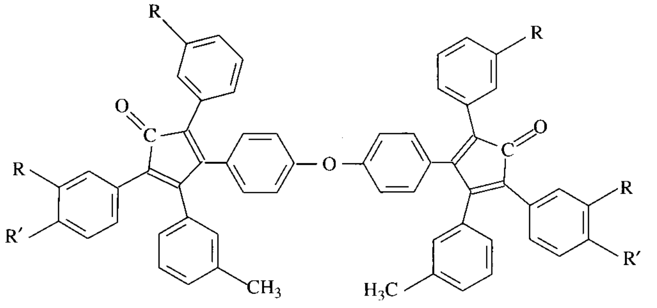
(6)

- where: -R= -R′ = -H; -R= -CH3, -R′= -H

Properties of the bis-cyclopentadienones thus obtained are given in Table 3.

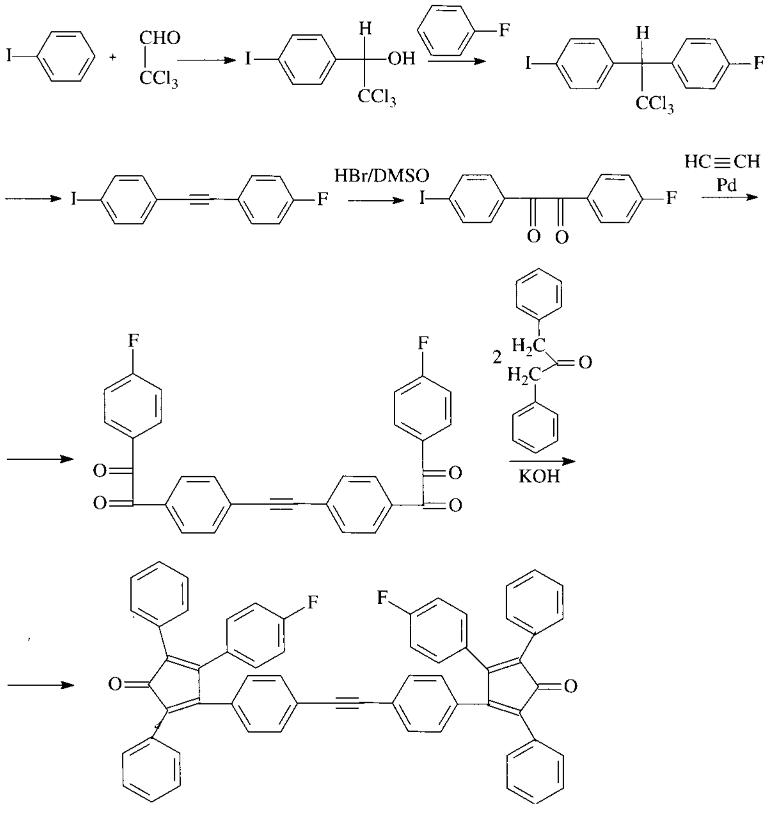
The bromine-containing bis-cyclopentadienone—4,4’(oxy-*p*-phenyl)bis[2(4-bromophenyl)-3-(3-methylphenyl)-5-phenylcyclopentadienone]2,2,3—was formed on treatment of the intermediate 4,4′-bis[(3-methylphenyl)-glyoxalyl]diphenyl ether with 1-phenyl-3(4-bromophenyl)acetone. Properties of the product are given in Table 3.

Table 3
Properties of bis-cyclopentadienones with the general formula



-R	R'	MP (°C)	Yield (%)	Reference
-H	-H	268	60	25
-CH_3	-H	192	58	25
-H	-Br	301	23.5	25

A fluorine-containing bis-cyclopentadienone—4,4′-bis[2,5-diphenyl-3(*p*-florophenyl)-cyclopentadien-1-on-4-yl]tolane—was prepared using a multi-step synthesis starting with chloral [26]:



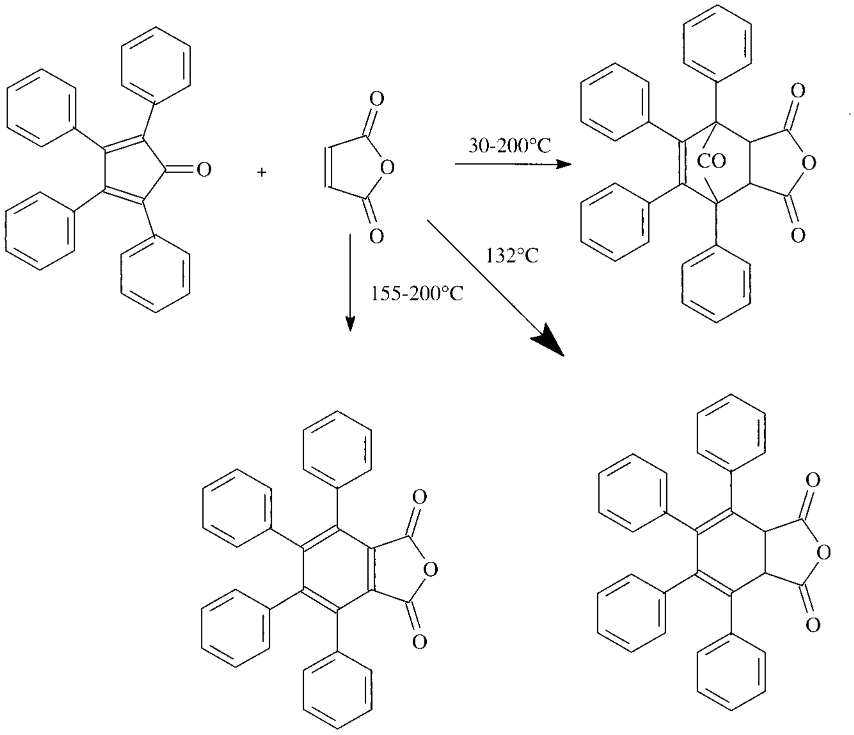
(7)

The non-melting target product was obtained with 63% yield. Its structure was elucidated using FT-IR-spectroscopy and elemental analysis.

Well-known Diels-Alder reactions of cyclopentadienones with double and triple carbon–carbon bonds [11] were used to transform bis-cyclopentadienones into other highly phenylated condensation monomers and high molecular weight polymers.

3. Transformation of bis-cyclopentadienones into highly phenylated condensation monomers

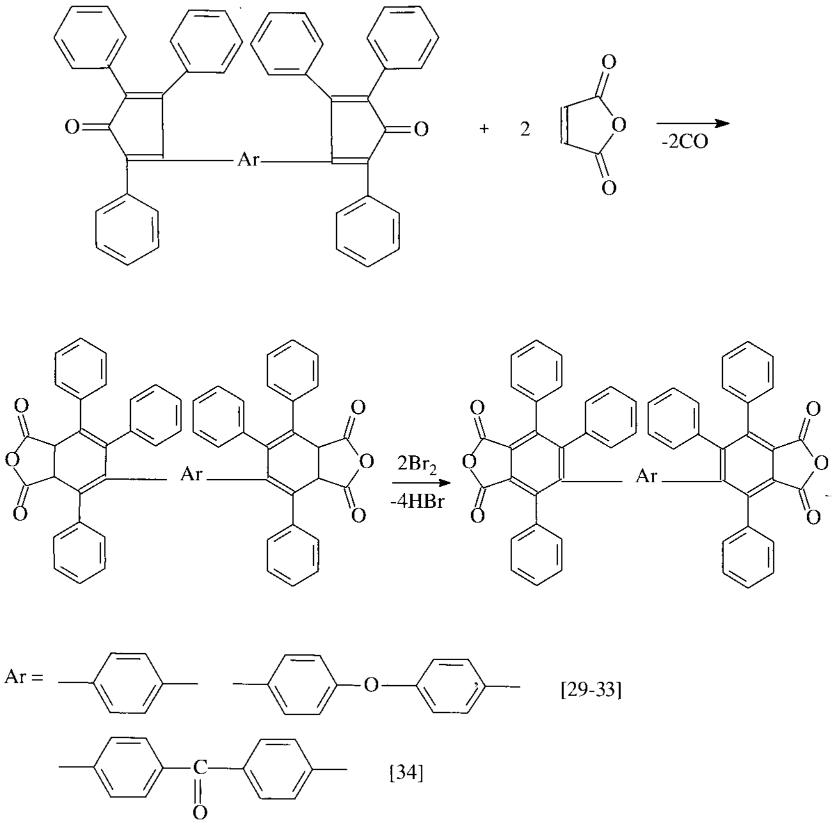
The reaction of a cyclopentadienone with maleic anhydride [11]



(8)

was successfully used to prepare hydroaromatic and aromatic tetracarboxylic acid dianhydrides.

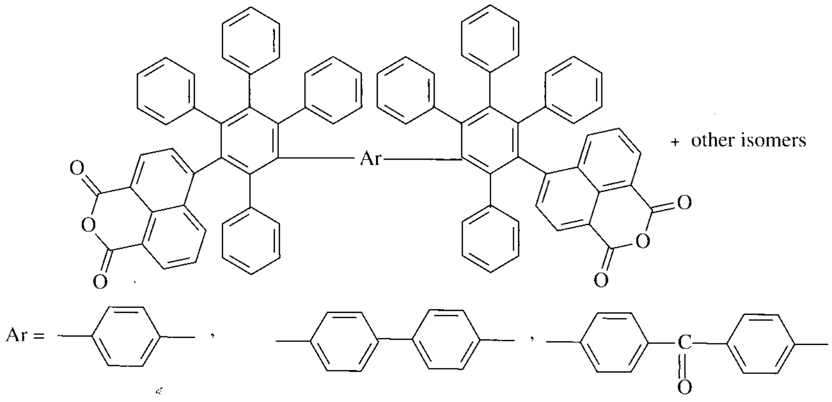
Various bis-cyclopentadienones prepared were converted to highly phenylated aromatic tetracarboxylic acid dianhydrides useful for the preparation of heterocyclic polymers [27,28]. The conversion was carried out according to the scheme [29–33]:



(9)

including Diels-Alder addition of maleic anhydride to a bis-cyclopentadienone and dehydrogenation of the adduct formed with bromine. All bis(phthalic anhydride)s were obtained in high yields; their properties are given in Table 4.

Diels-Alder addition of 4(phenylethynyl)naphthalic anhydride [33] to bis-cyclopentadienones with subsequent decarbonylation led to the formation of mixtures of isomers of bis(naphthalic anhydrides [32,34–36]:

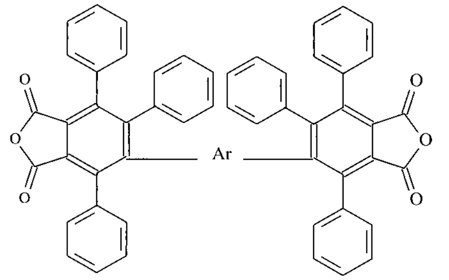


(10)

Some properties of the products are given in Table 5.

Highly phenylated aromatic diamines were prepared by the reaction of bis-cyclopentadienones with two-fold molar amounts of 4-nitrotolane under of Diels-Alder reaction conditions, and subsequent reduction of the dinitro compounds thus formed [37]:

Table 4
Properties of highly phenylated bis(phthalic anhydrides) with the general formula



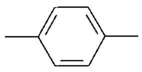
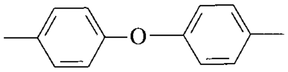
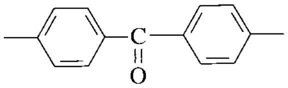
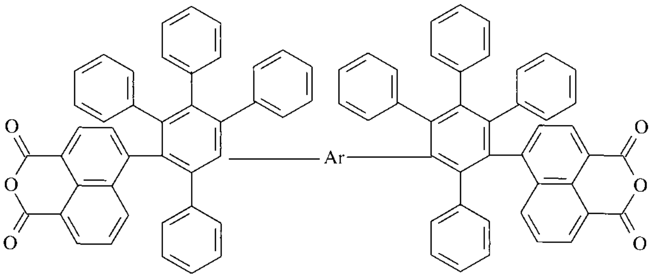
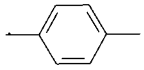
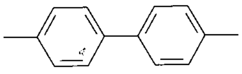
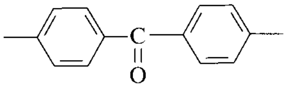
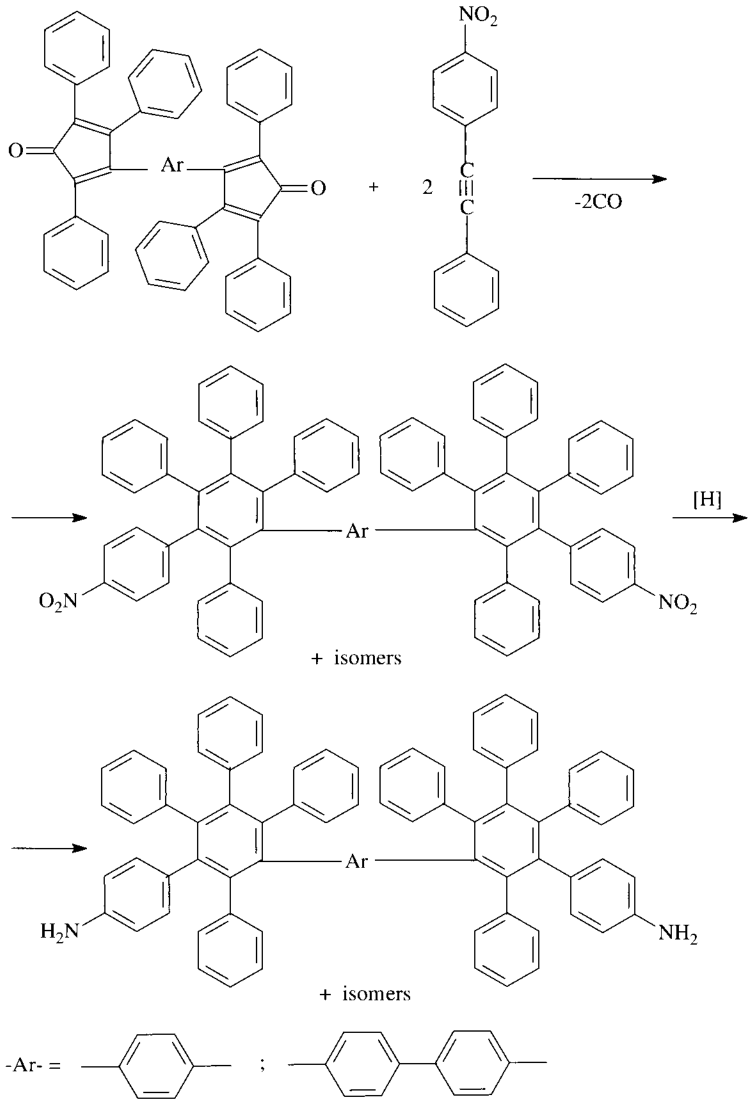
-Ar-	M.P. °C	Yield %	Ref.
	335-337 360-361	85	30,31
	250-255 330-332	75	30,31
	361-362	87	36

Table 5
Properties of highly phenylated bis(naphthalic anhydrides) with the general formula



+ isomers

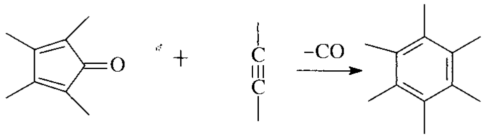
-Ar-	M.P. °C	Yield %	Ref.
	> 400	83	34, 36
	380-408 (DSC)	74	34, 36
	-	91	32, 34, 35



(11)

4. Synthesis and investigation of aromatic polymers based on bis-cyclopentadienones and their derivatives

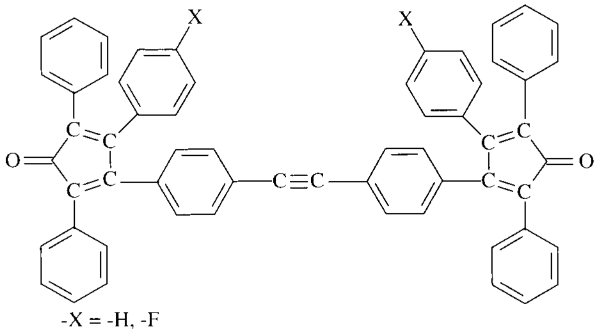
The usefulness of the reaction of cyclopentadienones with acetylenes lies in the direct formation of aromatic compounds



(12)

generally under mild conditions [11].

Bis-cyclopentadienones with the general formula:



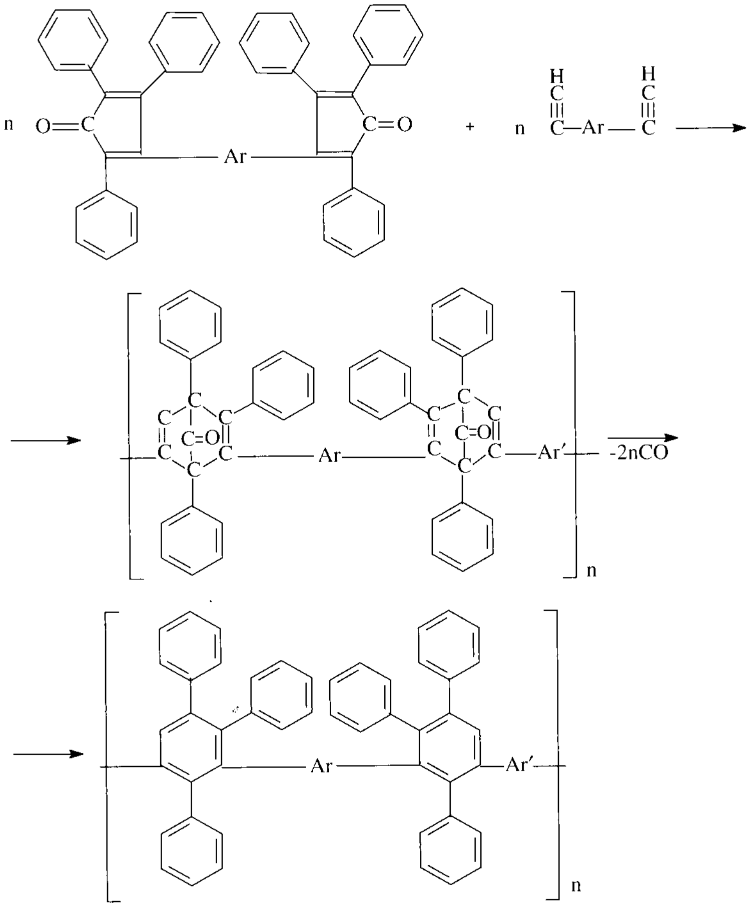
(13)

constitute A_2B monomers; their homoaddition reaction may (analogously to Refs. [38–40]) lead to hyperbranched polymers [41–51], i.e.-polyphenylenes with peripheral cyclopentadienone groups. Nevertheless, most attention has been paid to utilization of bis-cyclopentadienones for the preparation of linear phenylsubstituted polyphenylenes (PSPPs).

4.1. Linear PSPPs

4.1.1. PSPPs based on terminal diacetylenes

The most important Diels-Alder polyaddition reaction is the reaction of bis-cyclopentadienones with arylene-bis-acetylenes leading to the formation of PSPPs [52–55]:



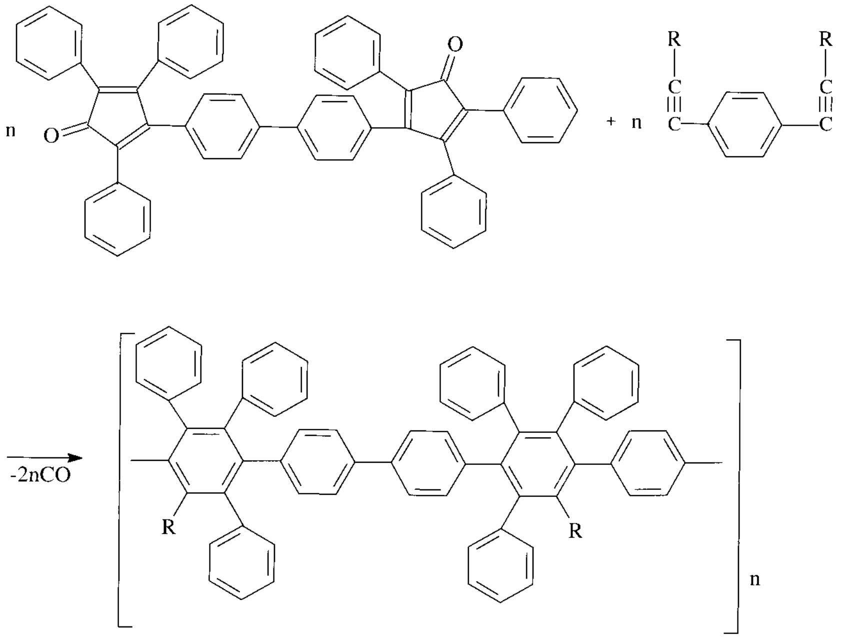
(14)

Comonomers of bis-cyclopentadienones—arylene-bis-acetylenes (diethynylarylenes)—can be prepared using various methods. Diethynylbenzenes were prepared by classical methods from the corresponding bis-methylketones [56].

In light of newer synthetic methods available for the preparation of aromatic acetylenes [57–61], they are most easily prepared by the Pd/Cu catalyzed coupling of (trimethylsilyl)acetylene with the corresponding aryl bromide or iodide, followed by removal of the protecting trimethylsilyl group. This procedure was used for the preparation of *m*-diethynylbenzene [62], 1-trimethylsilyl-3,5-diethynylbenzene [63], 1,3-diethynyl-2,4,5,6-tetraflurobenzene [64], 4,4′-diethynylbenzophenone [65], 2,5-diethynylthiophene [16,63] and 4,4′-diethynyltolane [20].

In addition, some heterocyclic diethynylarylenes-2(3-ethynylphenyl)-5-ethynylbenzothiazole [23], 2(3-ethynylphenyl)-6-ethynylbenzothiazole [23], *N*-3- ethynyl-4(3-ethynylphenoxy)-naphthalimide [23], 4(3-ethynylphenoxy)-*N*-(3-ethynylphenyl)-phthalimide [23], 2,2-bis[4(3-ethynylphenyl-*N*-phthalimide)]-hexafluoropropane [23]—were prepared using condensation reactions of ethynyl-containing compounds.

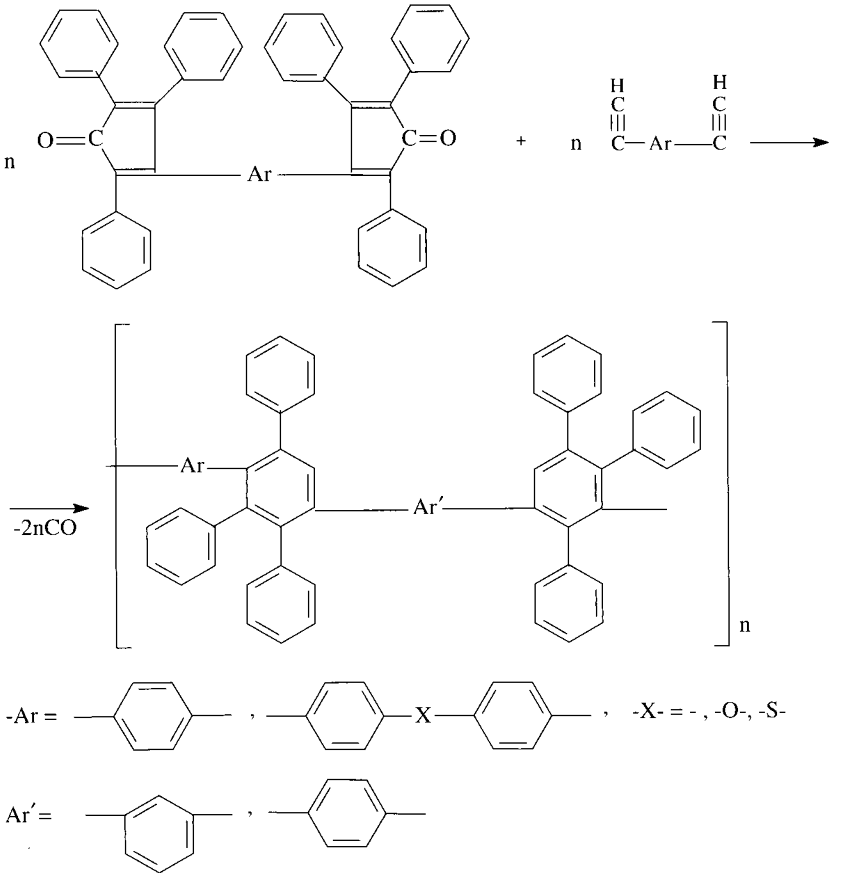
Ried and Freitag [66] reported the synthesis of PSPPs by the reaction of 4,4′′-bis(2,3,5-triphenylcyclopentadien-1-on-4-yl)diphenyl with a 1,4-diethynylbenzene in *β*-decalol,



(15)

but gave no details of the synthesis or target polymer properties.

Almost simultaneously, Stille and his co-workers [67–70] reported the preparation of PSPPs by the reaction of various phenylated bis-cyclopentadienones with *p*- and *m*-diethynylbenzenes [56] according to the scheme:



(16)

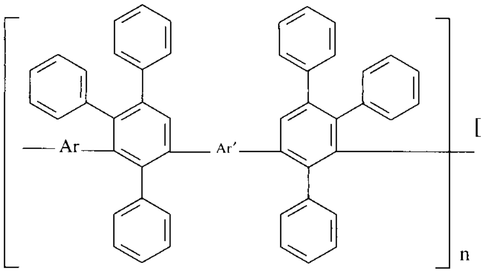
Syntheses of PSPPs were carried out in sealed tubes at 200-300°C for 24-50 h with toluene as the solvent.

The synthesis of polymers by the Diels-Alder reaction of bis-tetracyclones with diethynylbenzenes results in polymers containing either phenylated polyphenylene units or phenylene units linked by units such as oxygen or sulfur. In addition to the fact that these polymers exhibit the thermal stability (Table 6) associated with their polyaromatic structure, they are colorless and appreciably soluble in common organic solvents (benzene, toluene, chloroform, etc.). Thus these polymers were studied with respect to the effects of monomer balance and other polymerization conditions on molecular weight, the relationship of structure to some of the more obvious physical properties, the thermal stability and the mechanism of thermal degradation. In order to achieve proper monomer balance, great care was taken in the purification of the monomers. The stoichiometry required to achieve the highest molecular weight polymer required a 10% excess of bistetracyclone. This suggests either that there were impurities or that some side reaction upset the monomer balance. Severe polymerization conditions (350 °C, 48 h) in fact, gave lower molecular weight polymers ($\eta = 0.1$) and a small amount of black insoluble precipitate. These results suggest that there was considerable degradation, which interfered with monomer balance. Such degradation reactions at elevated temperatures are known for many tetracyclones [11].

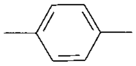
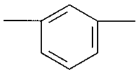
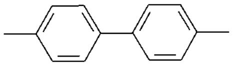
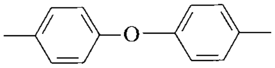
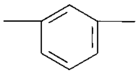
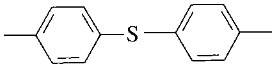
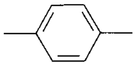
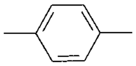
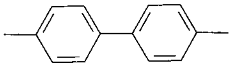
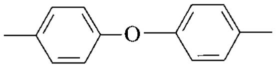
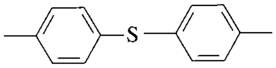
An unusual effect of concentration on molecular weight was also observed. An increase in monomer concentration caused an increase in viscosity. Although these results are difficult to explain, they are not without precedent for this type of polymerization [71,72].

The polymers obtained from these polymerizations showed very little differences in solubility. All the polymers were soluble to the extent of 10% in toluene and clear films could be cast from chloroform. Differential thermal analyses (DTA) of the polymers showed minimal changes in the slope of ΔH versus T_g, and no definite conclusion could be drawn as to the glass transition (Table 6). The polymers showed no crystallinity.

Table 6
Properties of phenylated polyphenylenes with the general formula



[67]

-Ar-	-Ar′-	η_{sp} dl/g (toluene)	M_n	TGA break, °C	DTA transition, °C
		0.32	1.73×10^4		
	"	0.26		550	120
		0.32		550	145
	"	0.20		550	
		0.73	3.28×10^4		
	"	0.46		550	-
	"	0.61		550	195
	"	0.40		550	150

Thermogravimetric analysis revealed that the polymers rapidly lose weight near 550 °C in air. However, in nitrogen, all the polymers show breaks near 575 °C, at which temperature the polymers lose approximately 30% of their total weight. Above 650 °C, the decomposition was slow (Fig. 1). The fact that all of the polymers showed nearly identical (30%) weight loss under nitrogen at the same temperature indicates that the one identical structural feature in all the polymers—the phenylated phenylene ring—was responsible. General properties of the PSPPs prepared under optimized conditions are given in Table 6.

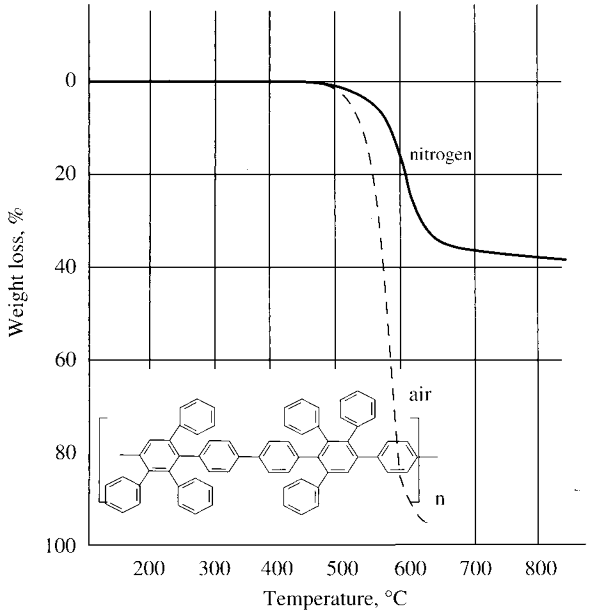


Fig. 1. Thermogravimetric analysis of phenylated polyphenylene.

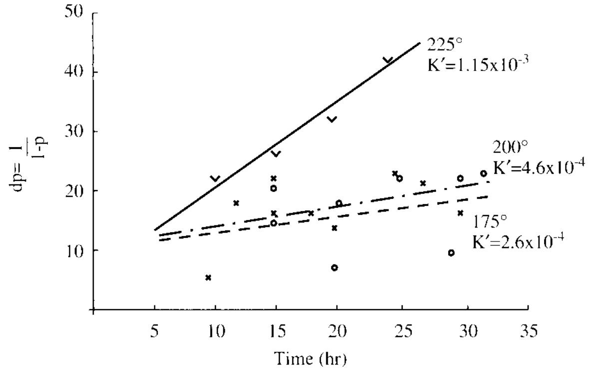


Fig. 2. Rates of polymerization at various temperatures [73].

4.1.2. Catenation and kinetics of the synthesis of PSPPs

Investigation of the polyaddition reaction kinetics [3,3′(oxidi-*p*-phenylene)bis(2,4,5-triphenylcyclopentadienone) and *p*-diethynylbenzene were used as reactants] demonstrated that these reactions follow a second-order rate law [73], and the rate constants at of 175, 200 and 225 °C were found to be 2.6×10^{-4}, 4.6×10^{-4} and 1.14×10^{-3} L/mol s, respectively. Rates of polymerization at various temperatures are given in Fig. 2. The Arrhenius activation parameters calculated from the rates constants were $\Delta H \neq 12.4$ kcal/mol and $\Delta S \neq -48$ e.u., consistent with a Diels-Alder reaction, which requires a low ΔH and a large negative ΔS [73].

One of the special properties of the PSPPs is their unusual solubility, mentioned above, in common organic solvents such as benzene, toluene and chloroform. This high degree of solubility can be attributed to the presence of the pendant phenyl groups [74,75]. However, a high degree of meta catenation in the polymer chain would also produce increased solubility, as has been observed with meta oligophenyls [76].

The type of catenation (meta or para) in synthesis of phenylated polyphenylenes was investigated [73] using a model reaction—the reaction of 3(4-biphenylyl)2,4,5-triphenylcyclopentadienone with 4-ethynylbiphenyl. The model reaction gave products in which the para/meta ratio (C_p/C_m) varied with the reaction temperature from 0.55 at 100 °C to 1.0 at 255 °C (Fig. 3). In the temperature range studied, para isomer comprises only about 30–50% of the product. Similar ratios of meta and para linkages are expected to occur along the

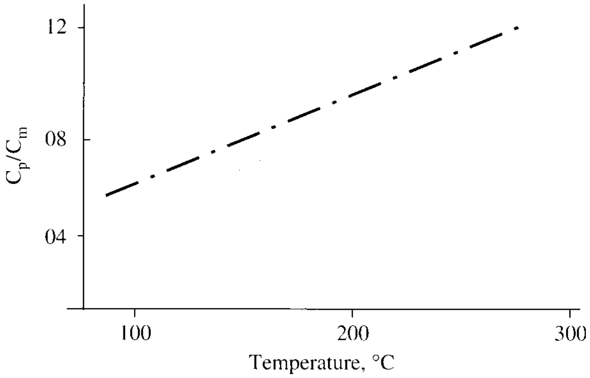


Fig. 3. Temperature dependence of the isomer ratio [73].

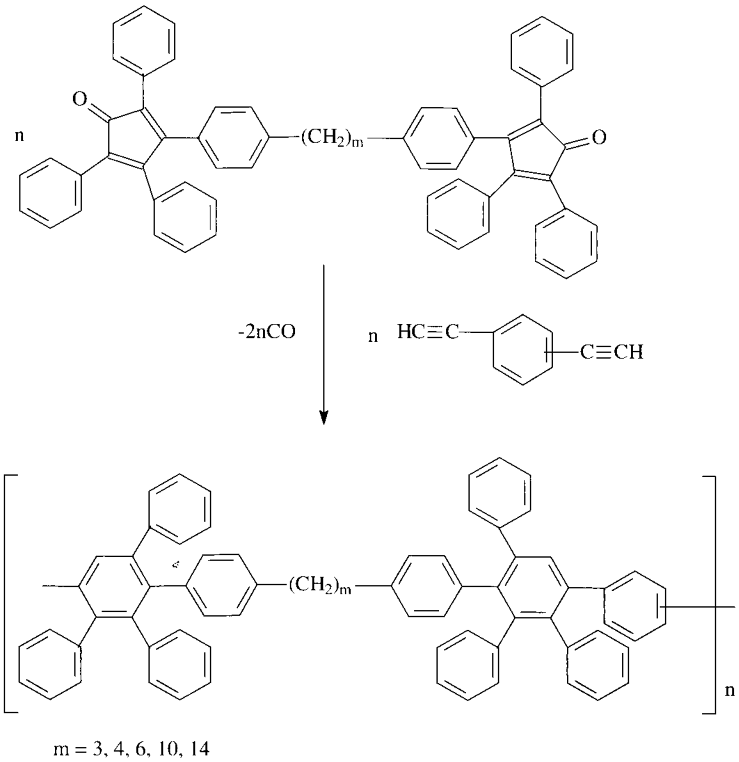
polymer chain backbones and add to the overall disorder of these polyphenylenes. This increased disorder can also account for the unusual solubility properties of PSPPs.

Diels-Alder reactions between 1,4-bis(2,4,5-triphenylcyclopentadienone-3-yl)benzene and either phenylacetylene (model reaction) or 1,4-diethynylbenzene (polymer formation) were studied using ^{13}C NMR- and ^{1}H NMR spectroscopy [77]. It was found that the main product in the model reaction is the *m,m'*-isomer (up to 83% yield). X-ray crystal structure analysis convincingly proved the structure of this isomer [77].

The presence of *m*-phenylene units in PSPP main chains results in relatively low Kuhn segments values (30–265 Å) determined for these polymers [78–80].

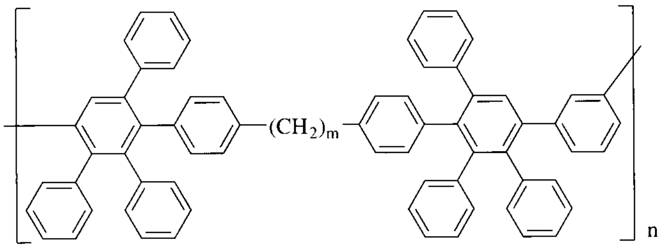
4.1.3. PSPPs containing alkylene chains

A series of polymers containing short blocks of phenylated polyphenylene units connected by alkylene chains have been prepared by the Diels-Alder reaction of *m*- or *p*-diethynylbenzene with tetraarylated biscyclopentadienones containing three, four, six, 10 and 14 methylenes [18,67,68]:



(17)

Table 7
Properties of alkylene-containing phenylated polyphenylenes with the general formula



[18, 68]

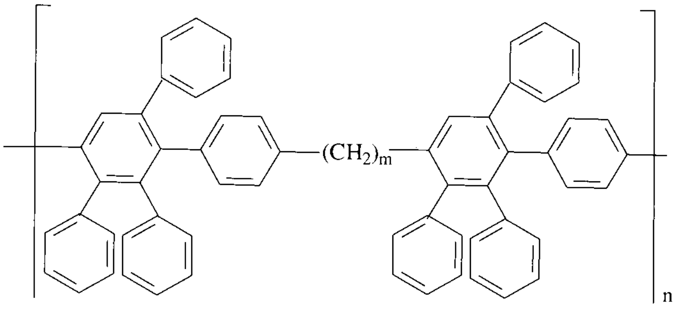
m	η_{sp}, dl/g (toluene) (25±0.5)°C	M_n	TGA decomp. pt, °C		Yield %
			nitrogen	air	
3	0.36	46,500	470	520	79
4	0.61	58,400	485	520	90
6	0.71	45,100	485	470	98
10	0.60	48,500	480	470	91
14	0.48	31,300	465	430	83

All polymerization reactions were carried out in sealed tubes at 225 °C for 24 h and 250 °C for 12 h with toluene as the solvent.

Light colored polyphenylenes were obtained in high yields (Tables 7, 8) and showed good solubility in common organic solvents. There was a slight increase in the solubility of the polymers as the length of the methylene segment of the polymer chain increased. The molecular weights of these polymer (Tables 7, 8) ranged from 30,000 to 60,000 and the intrinsic viscosities from 0.36 to 1.5. Clear films of all the polymers were cast from chloroform.

DTA of the polymers gave poorly resolved curves showing several changes in the slope of ΔT versus T. There was a slight trend for the temperature of the main second-order transition to decrease as the number of methylene groups increased in the polymer. The polyphenylenes connected by meta linkages had lower transition temperatures then the corresponding polyphenylenes with *para* linkages. Polymers showed no crystallinity as determined by an X-ray powder pattern. Thermogravimetric analyses (TGA) of the polymers (Tables 7, 8) revealed a loss of weight under nitrogen at 465–485 °C. A double break in the TGA curve was observed for all the polyphenylenes in air (Fig. 4). Some of the polymers showed greater thermal stability in air than in nitrogen, undergoing a weight loss at 500–520 °C. The second break in air occurred at 550–560 °C for

Table 8
Properties of alkylene-containing phenylated polyphenylenes with the general formula



[18, 68]

m	η_{sp} (toluene) (25±0.5) °C	M_n	TGA decomposition point[a] (°C)		Yield (%)
			Nitrogen	Air	
3	0.52	59,000	470	500	77
4	0.59	42,600	485	515	91
6	1.51	63,400	485	520	75
10	1.30	50,500	480	475	96
14	0.77	32,700	465	440	88

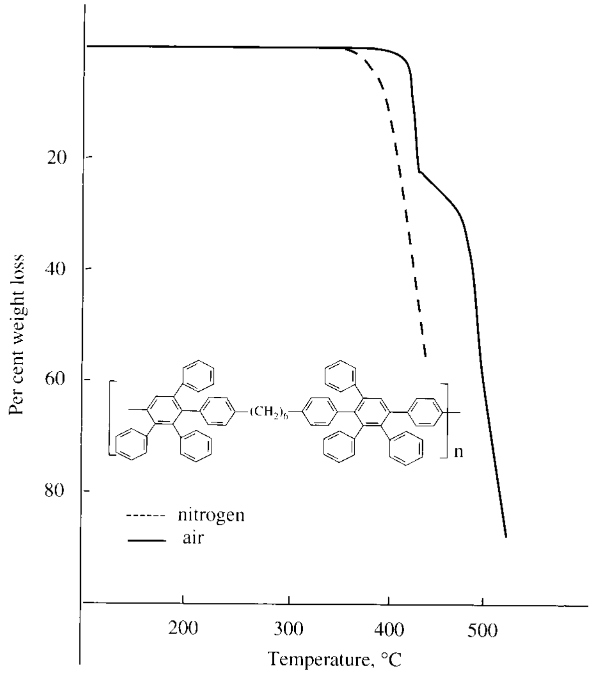
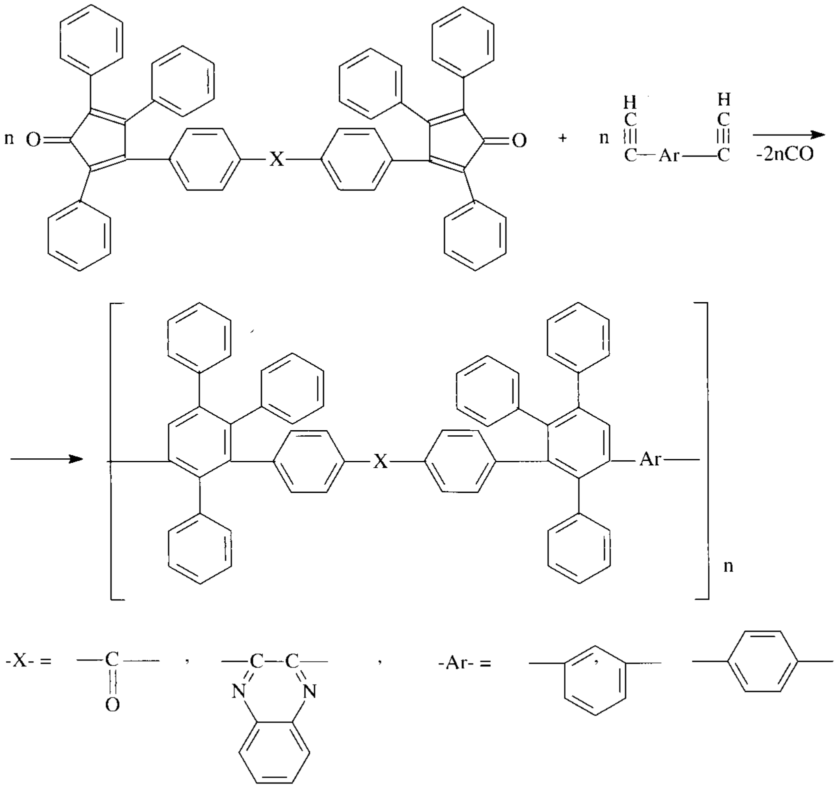


Fig. 4. Thermal gravimetric analysis of phenylated polyphenylenes containing hexametylene units [18].

all the polyphenylenes. This high thermal stability of polyphenylenes that contain aliphatic linkages in the backbone of the polymer chains is due to oxidation of methylenes in air forming carbonyl compounds.

4.1.4. PSPPs based on chloral-derived bis-cyclopentadienones

PSPPs based on chloral-derived bis-cyclopentadienones [17,21] were synthesized according to the scheme [21]:



(18)

Syntheses of these PSPPs were carried out in boiling 1,2,4-trichlorobenzene for 40 h under flowing argon [21]. Reactions proceeded homogeneously and led to the formation of target polymers completely soluble in toluene, chloroform, THF (tetrahydrofuran), DMSO (dimethylsulfoxide), DMAc (dimethylacetamide), NMP (*N*-methylpyrrolidone), etc.

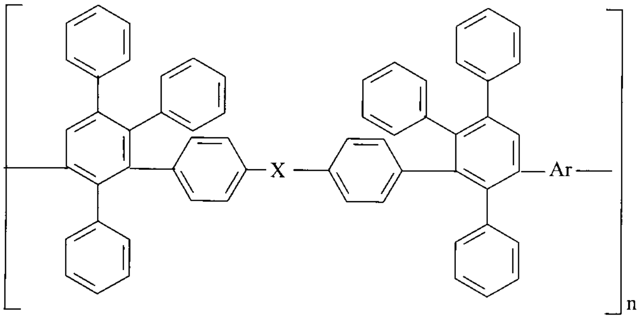
The average molecular weights determined by gel permeation chromatography (using PS calibration) and the reduced viscosities are consistent with the M_n. The molecular weights of the polymers prepared from quinoxal-2,3-diyl-containing bis-cyclopentadienone are considerably lower than those of the polymers based on carbonyl-containing bis-cyclopentadienone. Apparently, this is associated with the different reactivities of the bis-cyclopentadienones used. Molecular weights and η_{red} of the *m*-diethynylbenzene-based polyphenylenes are somewhat lower than for their analogs based on *p*-diethynylbenzene. Increased viscosities with *p*-linkages are due not only to increased M_n but also to the increased rigidity afforded by the *p*-linkages.

All the polymers listed in Table 9 show a Flory-type molecular mass distribution typical of polycondensation polymers (some increase in polydispersity as compared to the most probable is usually associated with the occurrence of macrocycles produced by polycondensation).

The glass transition temperature of PSPPs varies from 282 to 315 °C depending on the monomer structure. The thermogravimetric analysis data indicate that thermal stability of phenylated polyphenylenes is excellent (Table 10). The temperature for 10% weight loss of polymer in argon was in the range 539–666 °C, and in air varied from 610 to 643 °C (Table 10).

Good solubility and high molecular weights of the PSPPs resulted in good film-forming properties. Mechanical properties of the films are given in Table 10.

Table 9
Molecular-weight characteristics of phenylated polyphenylenes with the general formula



[21]

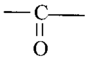
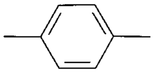
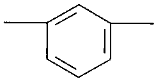
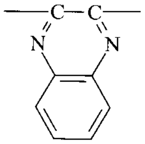
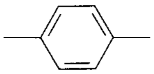
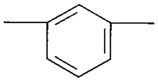
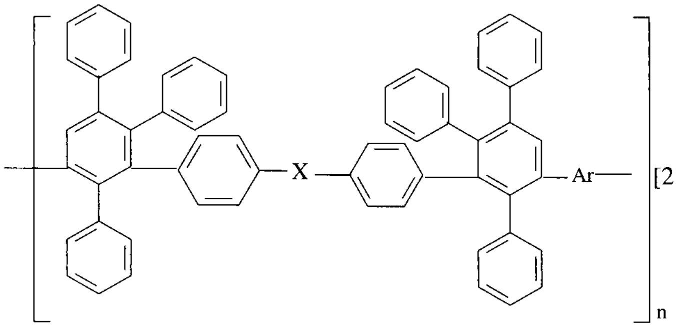
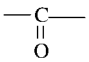
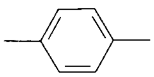
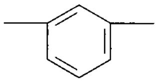
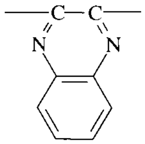
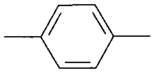
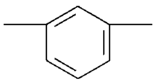
-X-	-Ar-	η_{red} dl/g	GPC		
			M_n x10^{-2}	M_w x10^{-2}	M_z x10^{-2}
 $-\underset{\underset{O}{\|}}{C}-$		0.82	592	2,076	4,801
"		0.52	271	782	1,450
		0.19	73	156	305
"		0.18	64	153	315

Table 10
Properties of phenylated polyphenylenes with the general formula

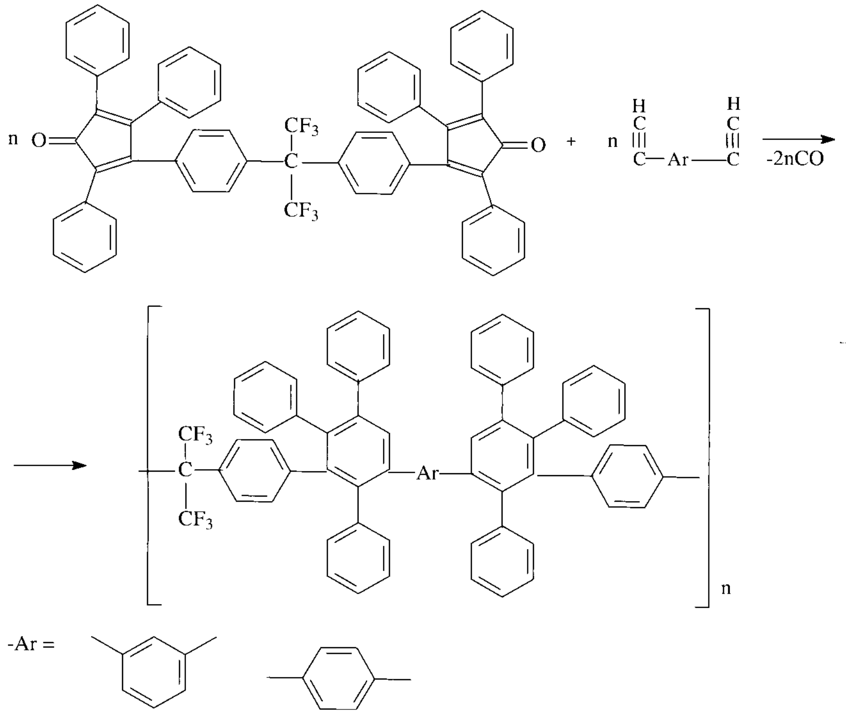


[21]

-X-	-Ar-	T_g °C	$T_{10\%}$ (TGA) ΔT= 4.5°K/min, air	Mechanical properties of films (25°C)	
				σ, MPa	ε, %
 $-\overset{\overset{\displaystyle O}{\|}}{C}-$		282	610	80.4	8.3
“		306	635	70.7	6.0
		315	625		
“		308	628		

4.1.5. PSPPs containing hexafluoroisopropylidene groups

PSPPs containing hexafluoroisopropylidene groups were prepared by the reaction of 1,1,1,3,3,3-hexafluoro-2,2-bis[2,4,5-triphenyl-3(p-phenylene)cyclopentadien-1-on]propane with m- and *p*-diethynylbenzenes [19,81] according to the scheme:



(19)

Synthesis of the PSPPs was carried out in boiling 1,2,4-trichlorobenzene over a 40 h period in a flow of argon; all reactions proceeded homogeneously and led to the formation of target polymers completely soluble in toluene, chloroform, THF, DMSO, DMAc, NMP, etc.

Molecular weights of the hexfluoroisopropylidene-containing PSPPs determined by GPC are presented in Table 11. These PSPPs have the unimodal most-probable molecular mass distribution.

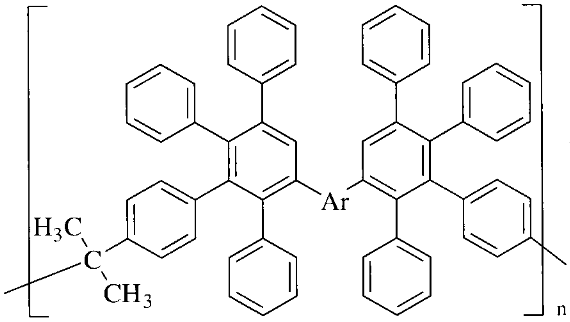
By comparing the molecular weights and the film-forming abilities of the polyphenylenes synthesized as indicated here and those described in Ref. [21], one may conclude the following: polymers with M_w not less than 8×10^4 form high strength films, but for polymers with $M_w < 4 \times 10^4$, it is impossible to cast high strength films. It appears that in the polyphenylenes of this family, some threshold value of molecular weight for film formation lies in the range $(4\text{–}8) \times 10^4$.

The glass transition temperatures of hexafluoroisopropylidene-containing PSPPs are 280–290 °C. The temperatures corresponding to 10% weight loss in argon and in air are 593–610 and 578–580 °C, respectively (Table 12).

4.1.6. PSPPs based on acetylene-containing bis-cyclopentadienones

PSPPs containing acetylenic groups in the polymer main chains were prepared by reaction of 4,4′-bis(2,3,5-triphenylcyclopentadien-1-on-4-yl)tolane [20,82] and 4,4′-bis[2,5-diphenyl-3-(*p*-fluorophenyl)cyclopentadien-1-on-4-yl]tolane [26] with isomeric diethynylbenzenes:

Table 11
Molecular weight characteristics of phenylated polyphenylenes with the general formula



[19, 81]

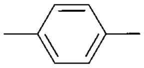
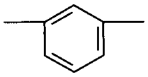
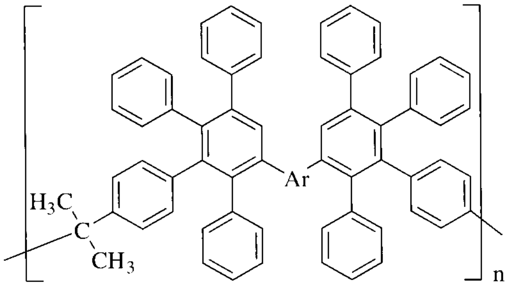
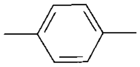
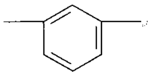
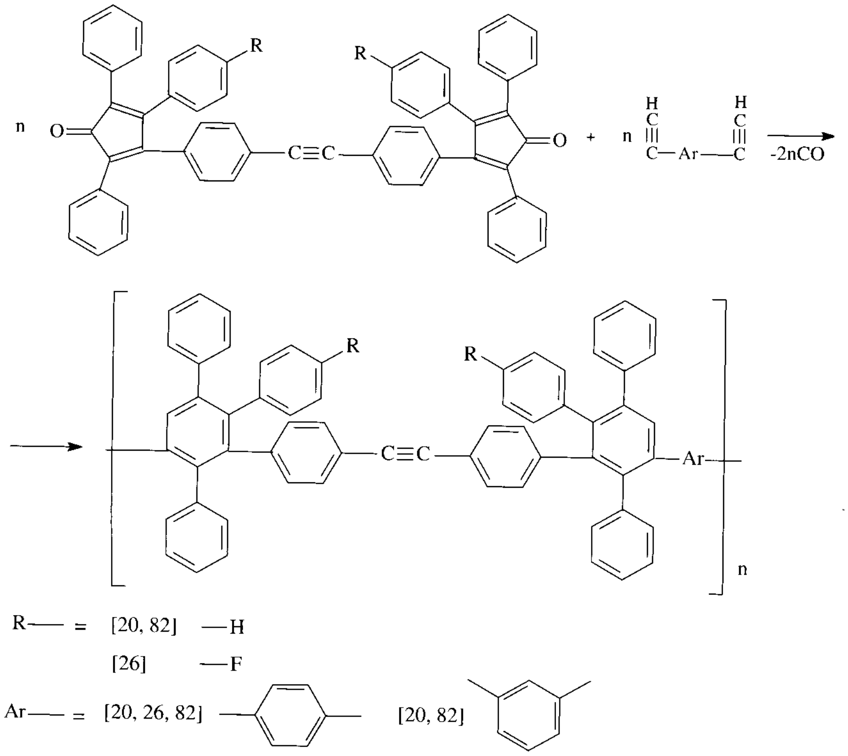
-Ar-	η_{red} dl/g 25°C	M_nx10^{-3}	M_wx10^{-3}	M_zx10^{-3}	M_w/M_n
	0.98	43.4	84.4	156.6	1.94
	0.57	10.8	21.1	35.7	1.95

Table 12
Some properties of phenylated polyphenylenes with the general formula



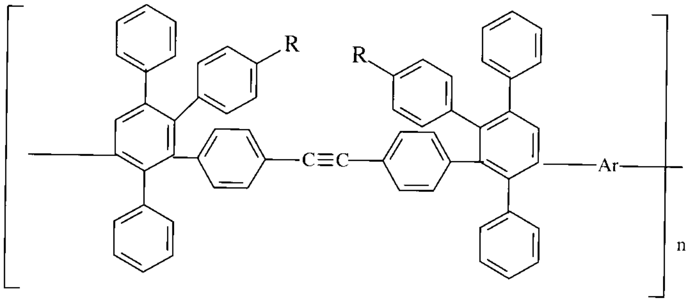
[19, 81]

-Ar-	η_{red}, dl/g	T_g, °C	$T_{10\%}$ (TGA) T=4.5°K/min, air	Tensile properties of films (25°C)	
				σ, MPa	ε, %
	0.98	290	580	50.1	3.4
	0.57	280	578	-	-

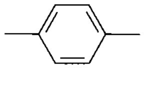
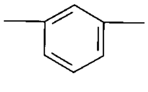
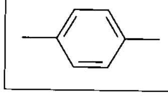


(20)

Table 13
Properties of acetylene-containing phenylated polyphenylenes with the general formula



[18]

-Ar-	-R-	$\eta_{red.}$ (DMF, 25°C) dl/g	Film properties (25°C)		Dielectric constant ε' at relative humidity	
			σ, MPa	ε, %	0%	59%
	-H	0.62	65.0	5.0	2.85	2.90
	-H	0.41	-	-	-	-
	-F	0.62	69.5	6.1	2.74	2.75

The acetylene-containing PSPPs were obtained in 1,2,4-trichlorobenzene under argon flow. The reactions were carried out at 220 °C for 40 h, with the reaction temperature increasing gradually from 120 to 220 °C over 4 h. When the temperature was increased quickly some gel formation was observed, apparently related to cross-linking via the triple bonds of the polymers. The resulting acetylene-containing PSPPs exhibited moderate viscosity characteristics (Table 13). All the polymers were soluble in aprotic solvents—DMF, DMSO, DMAc, NMP. 1,4-diethynylbenzene-based polymers formed films (Table 13).

The DSC thermograms of all the polymer samples exhibit broad exotherms, which reach maxima in the range 342–380 °C (Table 14). These exotherms are assigned to chemical transformations of acetylene-containing PSPPs macromolecules. These transformations include, for example, the formation of trisubstituted benzene rings, which function as interjunction fragments [83–86].

The temperature that marks the onset of deformation of the acetylene-containing PSPPs, as determined from thermomechanical curves (TMC), lies in the interval from 325 to 345 °C. Repeated heating of these samples to 450 °C leads to the disappearance of the exothermic peaks on the DSC thermograms, and the polymers become insoluble in organic solvents, although they retain deformability.

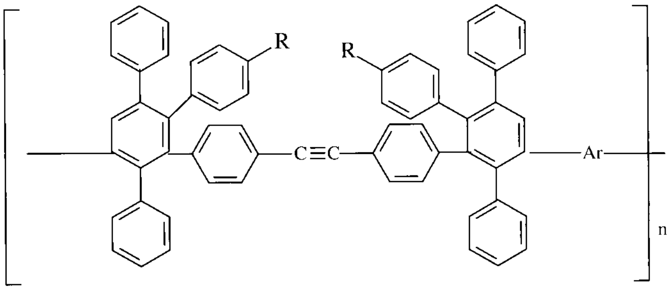
In fact, the smoothly proceeding reactions of acetylene-containing PSPPs syntheses may be considered as a new synthetic approach to the preparation of polyphenyleneethynylenes—polymers with promising electro-optical properties [87–90].

Along with *m*- and *p*-diethynylbenzenes, 4,4′-diethynylbenzophenone [25,94] and 4,4′-diethynyltolane [20] were also used for preparation of PSPPs.

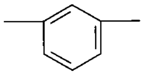
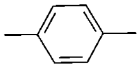
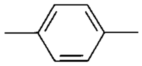
4.1.7. *PSPPs based on 4,4′-diethynylbenzophenone*

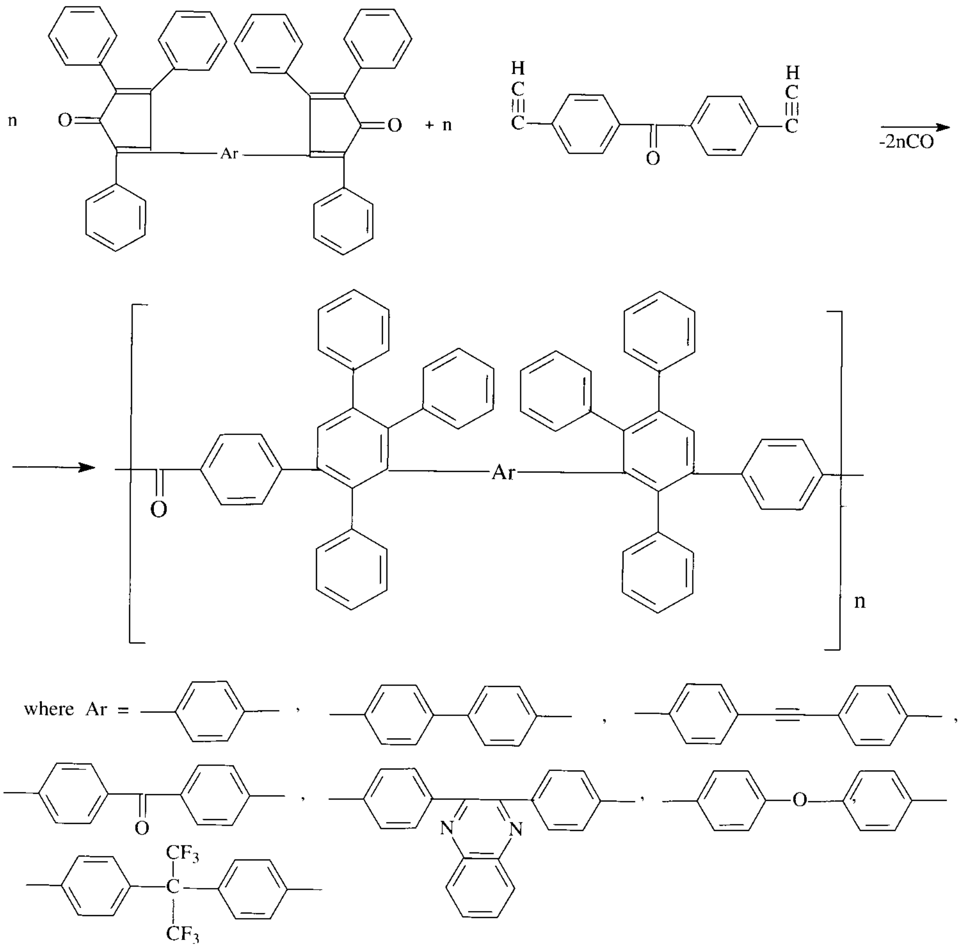
The syntheses of phenylated polyphenylenes using 4,4′-diethynylbenzophenone monomer were carried out according to the scheme [91]:

Table 14
Properties of acetylene-containing PSPPs with the general formula



[18]

-R	-Ar-	Temperature, °C		
		Onset of deformation according to TMS	Maximum in DSC curve	10% weight loss, $\Delta T = 4.5°\mathrm{min}^{-1}$
-H		328	342	570
-F		352	352	583
-H		345	347	590



(21)

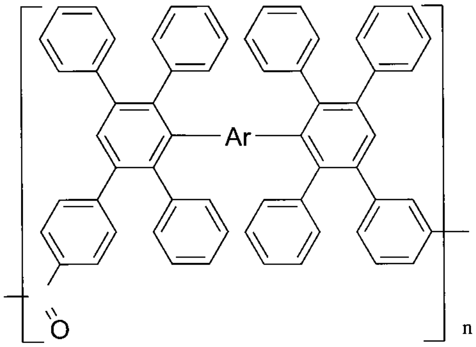
The synthesis was carried out in 1,2,4-trichlorobenzene at 130–140 °C for 7 h, that is, under milder reaction conditions compared to the synthesis of PSPPs based on diethynylarylenes devoid of electron-withdrawing groups [67–70]. The reactions were homogeneous and produced polymers with reduced viscosities of 0.51–0.89 dl/g, corresponding to $M_n = (8.8-69.2) \times 10^3$, $M_w = (38.4-712.5) \times 10^3$, respectively, and $M_w/M_n = 3.06-10.57$.

4,4-Diethynylbenzophenone-based PSPPs are soluble in toluene, *p*-xylene, methylene chloride, chloroform, *m*-cresol, DMF, DMSO, NMP, etc.

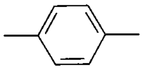
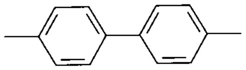
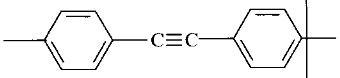
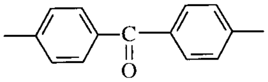
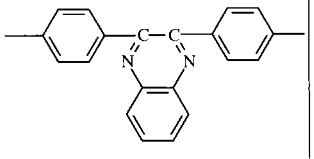
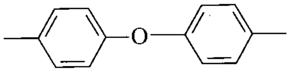
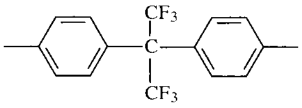
The good solubility of PSPPs provided an opportunity to prepare films from these polymers. The mechanical properties of the films are shown in Table 15. The tensile strength and elongation at break of the examined films are within the ranges 68.1–91.9 MPa and 65–49%, respectively.

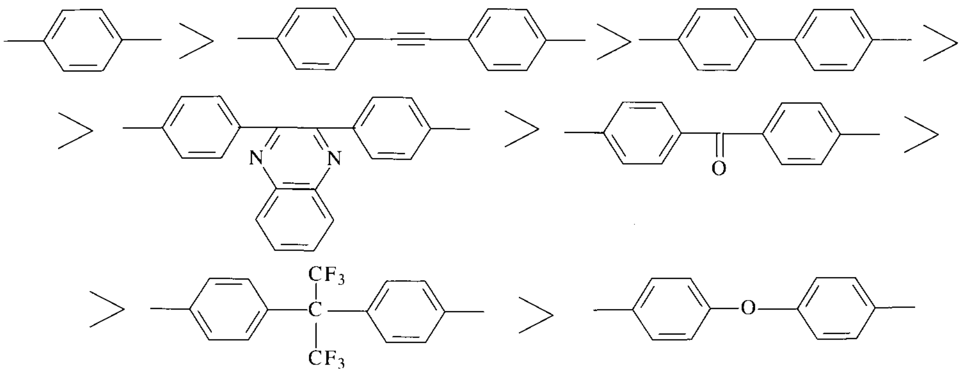
The glass transition temperatures of PSPPs were estimated by thermomechanical analysis, and the results are presented in Table 15. Values of T_g range from 258 to 330 °C depending on the structure of the bis(cyclopentadienone) fragment; T_g decreases in the sequence

Table 15
Properties of phenylated polyphenylenes with the general formula



[91]

-Ar-	η_{red}, (m-cresol) 25°C dl/g	M_n	T_g °C	$T_{10\%}$ (TGA) air	Film properties (25°C)	
					σ, MPa	ε, %
	0.88	69,200	340	600	79.8	16.5
	0.62	20,180	305	610	91.9	17.7
	0.51	19,235	330	591	68.1	6.4
	0.48	48,300	295	643	74.2	49.0
	0.29	800	301	630	-	-
	0.73	30,890	258	598	76.7	7.5
	0.89	38,680	285	570	78.0	6.6

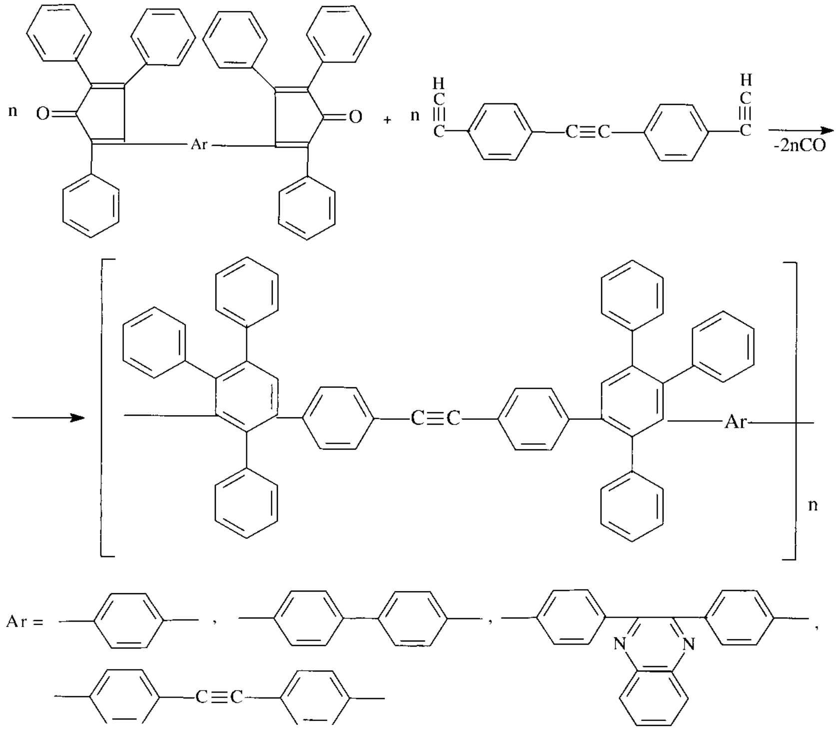


(22)

Thermal and thermo-oxidative stabilities of the polymers were estimated by TGA. As follows form Table 15, all these polymers display high thermal stability ($T_{10\%}$ is 570–643 °C in air , and 630–658 °C in argon).

4.1.8. PSPPs based on 4,4′-diethynyltolane

The synthesis of 4,4′-diethynyltolane-based PSPPs were carried out according to the scheme [20]:



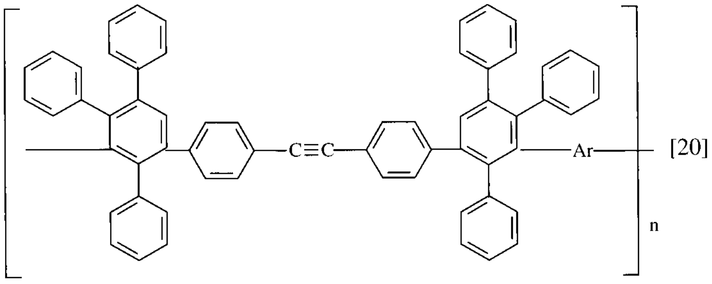
(23)

All reactions were carried out in 1,2,4-trichorobenzene at 220 °C for 40 h, the reaction temperature was increased gradually (from 120 to 220 °C over 4 h). When the temperature was increased quickly, some gel formation was observed. Extensive evolution of CO was observed, and the solution color changed from deep red to yellow. All reactions were carried out under homogeneous conditions and led to the formation of the target polymers (Table 16) in almost quantitative yields.

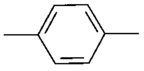
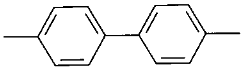
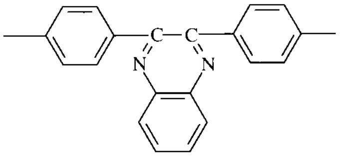
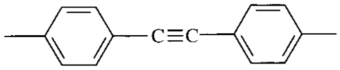
All acetylene-containing PSPPs dissolve in NMP, DMF and [except for the polymer based on 4,4′-bis(2,3,5-triphenylcyclopentadien-4-yl-1-on)tolane] in DMSO, *m*-cresol, THF and chloroform; reduced viscosities in NMP are 0.41–0.91 dl/g.

Films were cast, demonstrating acceptable mechanical properties (Table 16), from solutions of all the acetylene-containing PSPPs in chloroform and NMP [except for the polymer based on 4,4′- bis(2,3,5-triphenylcyclopentadien-4-yl-1-on)tolane].

Table 16
Properties of phenylated polyphenyleneethynylenes with the general formula



[20]

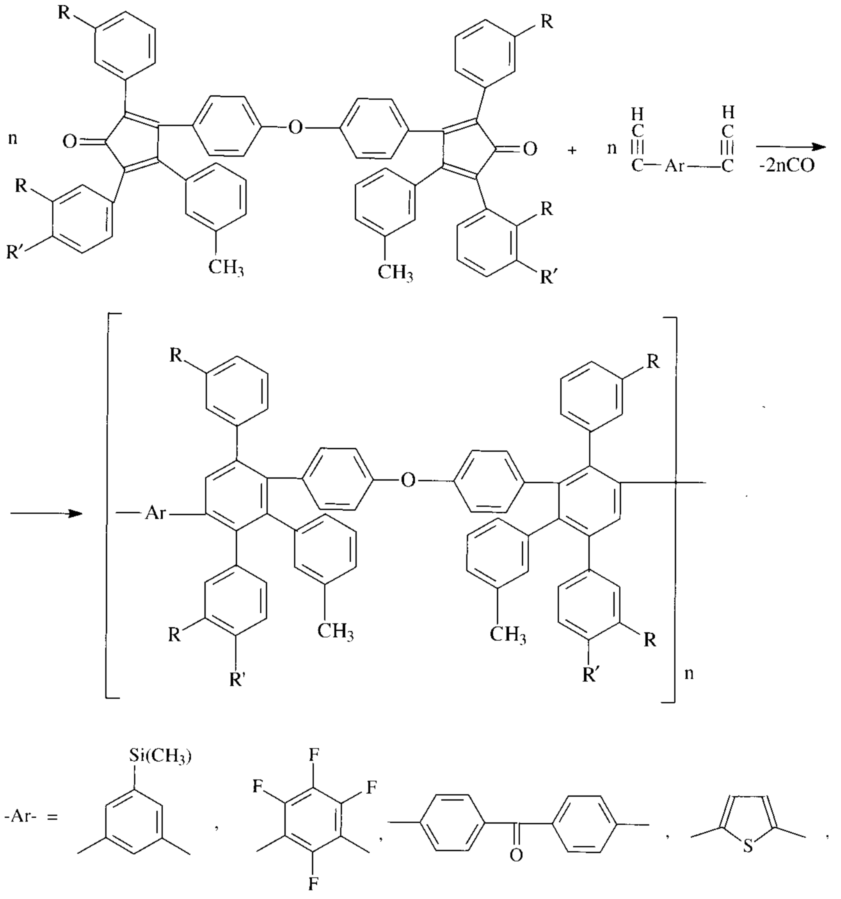
-Ar-	η_{red} (NMP, 25°C), dl/g	Film properties		T_g, °C	$T_{10\%}$ (TGA) ΔT =10°/min, air/Ar
		σ, MPa	ε, %		
	0.91	69.8	8.1	340	564/614
	0.86	70.9	8.1	335	575/635
	0.41	-	-	318	569/621
	0.68	72.0	9.3	329	580/645

Thermal properties of the polymers were investigated by DSC, TMA and TGA. The softening temperatures, as demonstrated by the thermomechanical curves, are in the range 318–340 °C (Table 16). DSC curves of all the polymers have broad exothermic peaks which reach maxima at 352–425 °C. These exotherms are due to cross-linking via triple bonds. Thermal treatment of the polymers leads to an increase of their softening temperatures to 329–370 °C. The thermally treated polymers are insoluble in organic solvents, indicating the formation of cross-linked structure.

DTGA of the acetylene-containing PSPPs in air and in Ar demonstrated a temperature of 10% weight loss of 605–670 °C (argon) and 520–595 °C (air). It is interesting to note that PSPPs containing acetylene groups are more thermally stable than PSPPs free of acetylene groups. The formation of cross-linked structure resulting from reactions via acetylenic groups probably leads to a decrease in the intensity of the degradation process.

4.1.9. PSPPs containing tolyl side groups

PSPPs containing tolyl side groups were prepared according to the scheme [25]:



(24)

R = R′ = H ; R = CH_3, R′ = H

Polyaddition reactions were carried out in Schlenk tubes at 200 °C for 24–40 h using cyclohexylbenzene as the solvent. All reactions proceeded homogeneously and resulted in PSPPs combining relatively high molecular weights (GPC, Table 17) with solubility in organic solvents—toluene, xylene, THF, *p*-dioxane, chloroform, chlorbenzene, DMF, NMP, etc.

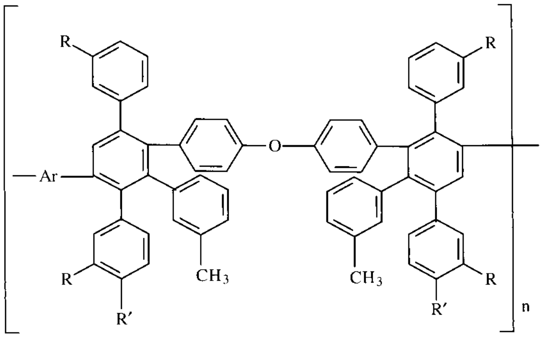
The polymers formed thick coherent films on a variety of substrates (silicon, quartz, aluminum oxide). Most of the polymers exhibited a weak glass transition temperature in the range 245–300 °C. As expected, the thermal stability of the polymers is higher in argon than in air with a difference of 25–50 °C in degradation temperatures.

In general, polymers without methyl groups had better thermal stability than methyl-containing polymers, due to easy oxidation of the methyl groups. Several of the polymers containing methyl groups showed weight gains of 3–4% in air at temperatures above 350 °C, owing to the oxidation of the pendant methyl groups [25].

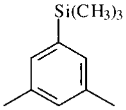
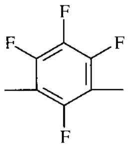
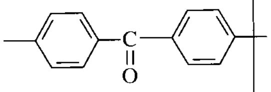
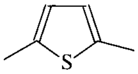
4.1.10. Polyphenylenes containing diphenyl ether and diphenyl thioether side groups

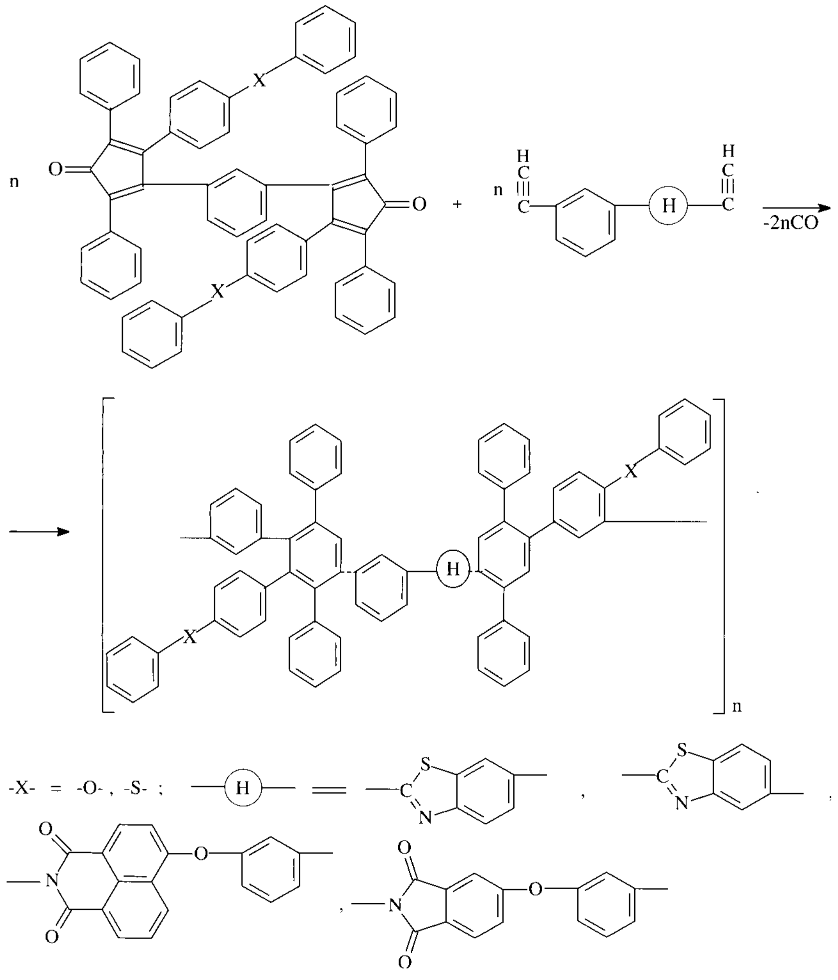
PSPPs containing diphenyl ether and diphenyl thioether side groups, along with phenyl substituents, were prepared according to the scheme [23]:

Table 17
Properties of phenylated polyphenylenes with the general formula



[25]

-Ar-	-R	-R′	M_n	M_w	M_w/M_n	T_g °C	$_{10\%}$, °C	
							air	argon
	-H	-H	72	39	1.8	80	514	27
“	$-CH_3$	-H	56	35	1.6	55	346	67
	-H	-H	109	53	2.0	85	490	34
“	$-CH_3$	-H	350	140	2.5	-	370	99
	-H	-H	148	53	2.8	275	483	101
“	$-CH_3$	-H	185	53	3.5	-	383	10
	-H	-H	79	19	4.2	255	515	527



(25)

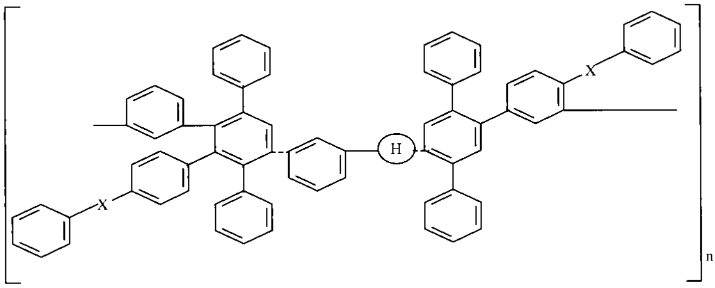
The Diels-Alder polymerization of the appropriately substituted bis-cyclopentadienone monomers with the various diacetylenic monomers were carried out in sealed tubes with 1,2,4-trichlorobenzene as the solvent. All polymerizations were conducted at 220 °C for 18 h, followed by heating at 240 °C for an additional 24 h. Polymer synthesis reactions proceeded homogeneously and resulted in polymers soluble in hydrocarbons (benzene, toluene, xylene), chloroform, DMAc, etc. General properties of the polymers prepared are listed in Table 18. Tough flexible films were cast from 1% solution of the polymers in chloroform.

The glass transition temperatures for the polymers are in the range of 230–280 °C; incorporation of diphenyl ether groups instead of phenyl groups lowers the T_g about 50 °C. It is interesting to note that equivalent lowering of the T_g has been shown to occur for the as-triazine and quinoxaline polymer systems [92].

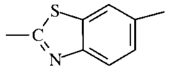
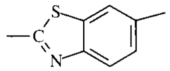
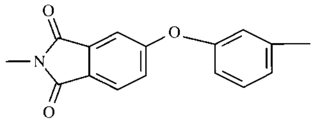
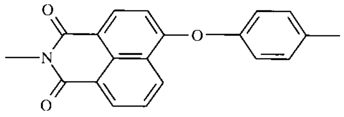
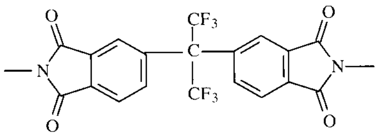
Thermogravimetric-mass spectral analysis conducted under vacuum on a phenylphenoxy- pendant benzothiazole polyphenylene showed that degradation commences at 500 °C and continues to the highest temperature studied, 850 °C. There are basically two regions of volatile product evolution, 600 and 750 °C. The major volatile products released at 600 °C include benzene, biphenyl, phenol and phenyl ether, with the highest molecular weight product identified as triphenyl. The higher temperature cracking processes (750 °C) release methane, carbon monoxide and hydrogen.

Along with terminal diacetylenes, internal diacetylenes [14,25,36,93] were used for the preparation of phenylated polyphenylenes. Internal diacetylenes are less reactive than terminal diacetylenes but are more readily available.

Table 18
Properties of the arylated polyphenylenes with the general formula



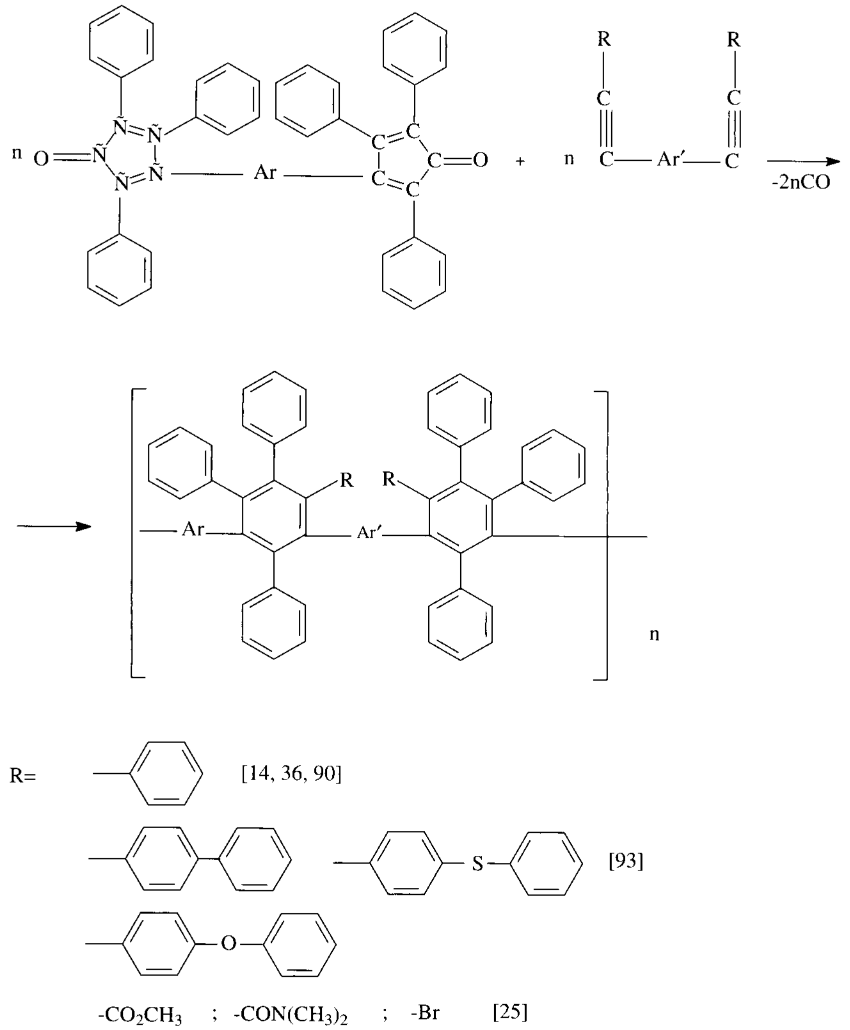
[23]

Ⓗ	-X-	[η]	T_g[a]	Isothermal gain, %[b]
	-O-	0.30	282	50
“	-S-	0.35	255	80
	-O-	0.45	269	55
“	-S-	0.29	266	35
	-O-	0.61	238	80
“	-S-	0.57	233	89
	-O-	0.54	273	44
“	-S-	0.48	264	29
	-O-	0.55	240	86

[a] Glass transition temperature as determined by DSC, Δ T – 10°/min
[b] % weight retained (isothermal aging in air, 650°F for 200 h)

4.1.11. PSPPs based on internal diacetylenes

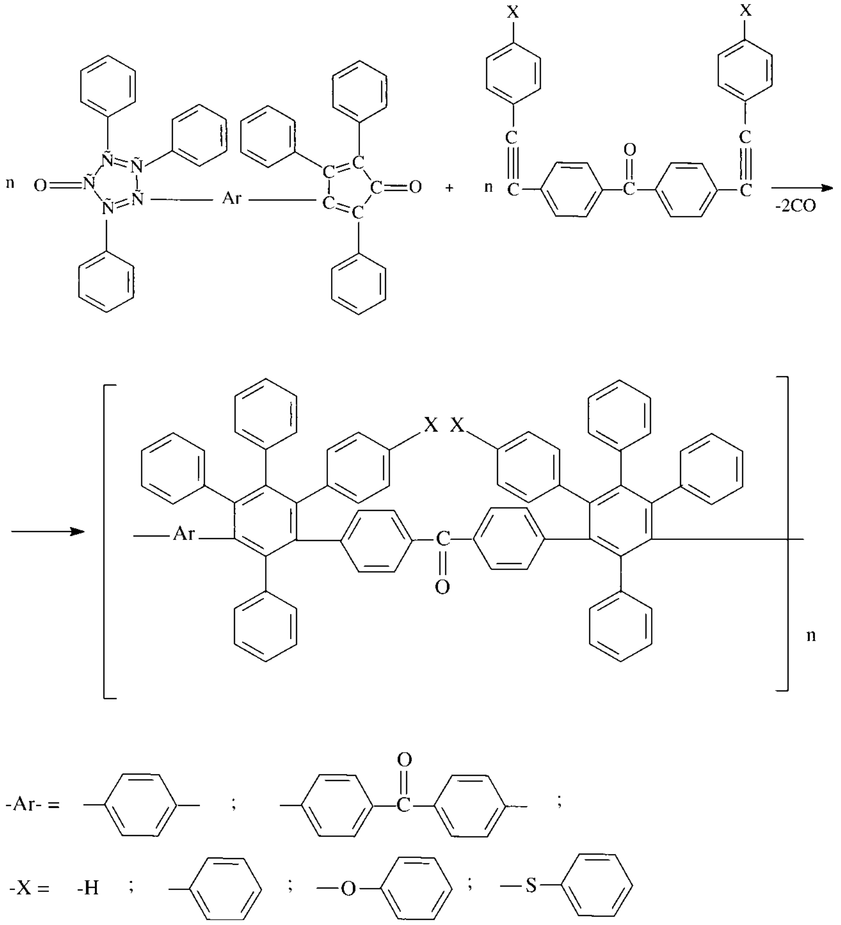
The synthesis of phenylated polyphenylenes using internal diacetylenes was carried out according to the scheme:



(26)

Although Ried and Freitag [66] suggested the use of disubstituted acetylenes for polymerization with bis-cyclopentadienones, the first such example was reported by Wrasidlo and Augl [14] who condensed the *p*-phenylene derivative with 1,4-bis(phenylethynyl)benzene at 240 °C for 2 h followed by 330 °C for 4 h to produce a polyphenylene with four phenyl groups on every other aromatic ring of the polymer. Under these conditions a polymer with intrinsic viscosity of 0.34 was obtained that was stable at 550 °C and lost 38% of its weight at 800 °C.

Polymers demonstrating moderate molecular weights were prepared according to the scheme [93]:

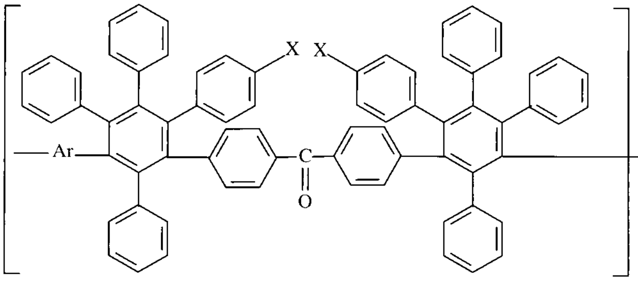


(27)

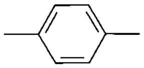
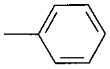
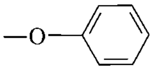
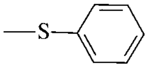
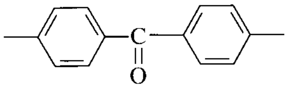
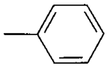
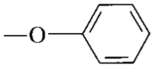
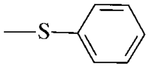
Reactions carried out in boiling 1,2,4-trichlorobenzene led to the formation of polyphenylenes soluble in toluene, xylene, chloroform and other organic solvents. Properties of the polyphenylenes obtained are given in Table 19.

Polyphenylenes containing CO_2CH_3, $CON(CH_3)_2$ and Br groups along with phenyl substituents were prepared according to the scheme [25]:

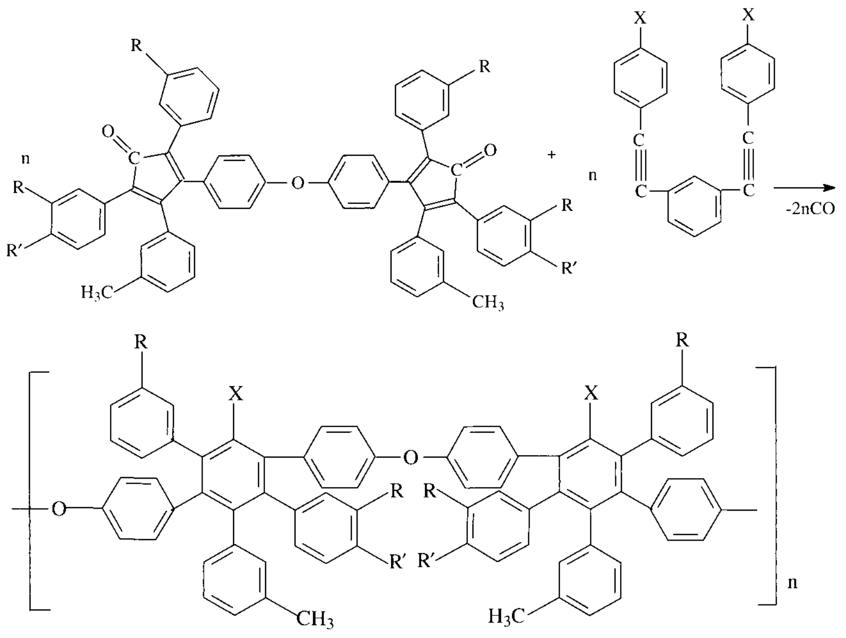
Table 19
Properties of arylated polyphenylenes with the general formula



[93]

-Ar-	-X	η_{red} (DMF, 25°C) dl/g	T_g[a]	$T_{10\%}$		Mnx10^{-3}
				air	argon	
	-H	0.44	365	565	642	24.30
"		0.50	328	592	639	16.30
"		0.51	276	613	629	9.20
"		0.43	229	530	581	13.10
	-H	0.51	310	558	628	22.60
"		0.53	295	601	633	32.80
"		0.48	240	590	615	23.80
"		0.41	215	536	588	7.60

[a] Glass transition temperature as determined by DSC, ΔT - 10°/min



(28)

-X = CO_2CH_3 -$CON(CH_3)_2$ -Br

-R = R` = -H -R = -$CH_3$ -R` = -H -R = -H -R` = -Br

Polymerization reactions were carried out in Schlenk tubes at 200 °C for 24–30 h using cyclohexylbenzene as the solvent. Reactions proceeded homogeneously and led to the formation of polyphenylenes completely soluble in toluene, xylene, THF, chloroform, chlorobenzene, DMF, NMP. Properties of the polyphenylenes are listed in Table 20.

Relatively low molecular weights of the polymers are attributed to the decreased reactivity of internal diacetylenes and their thermal instability under the polymerization reactions conditions, resulting in deviation from exact stoichiometry.

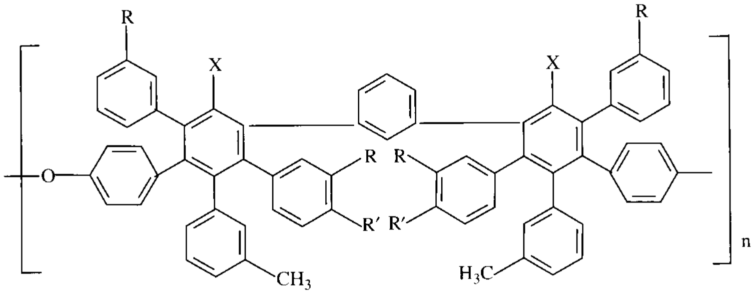
4.2. Synthesis of linear phenylated polyimides by the reaction of bis-cyclopentadienones with N,N′-bis-maleimides

Although aromatic polyimides retain usable properties at 300 °C for months [1] and withstand exposure of a few minutes to temperature well over 500 °C, their applications have been limited. This is due to their insolubility which, combined with their high transition temperatures make then extremely difficult to fabricate. In fact, these polymers are processed in the form of their polyamic acids precursors, which are then thermally or chemically converted to the imide structure. Processing is still difficult, however, because the precursors are thermally and hydrolytically unstable and because water is evolved during the cure process.

One approach to obtaining solubility in linear aromatic polymers has been the introduction of pendant phenyl groups along the polymer backbone [5,74,94].

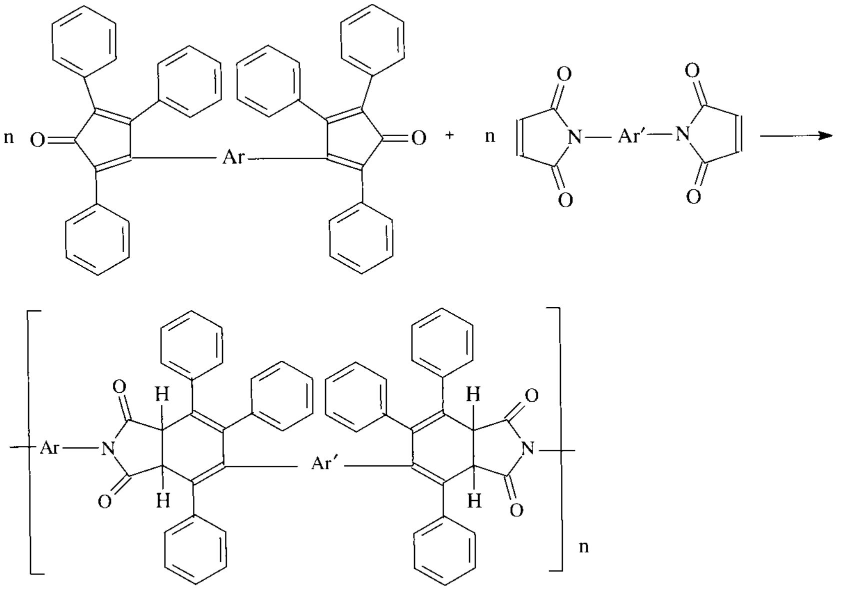
Diels-Alder reaction of tetracyclone with maleimide [11] is suitable as a mode of propagation in the synthesis of phenylated polyimides [71,95–97]. The reactions of 3,3′(oxydi-*p*-phenylene)-bis(2,4,5-triphenylcyclopentadienone) and 3,3′(*p*-phenylene)bis(2,4,5-triphenylcyclopentadienone) with *N,N*′-o, -*m*- and *p*-phenylene-bismaleimides yield polydihydrophthalimides [97]:

Table 20
Properties of polyphenylenes with the general formula



[25]

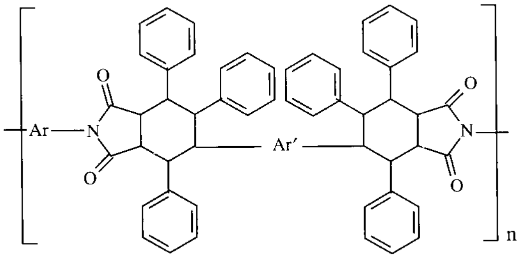
-R	-R′	-X	M_n ($x10^{-3}$)	M_w ($x10^{-3}$)	M_w/M_n	T_g °C	$T_{10\%}$, °C	
							air	argon
-H	-H	$-CO_2CH_3$	58	28	2.1	-	474	504
CH_3	-H	"	60	32	1.9	265	340	368
-H	-Br	"	86	32	2.7	275	400	432
-H	-H	$-CON(CH_3)_2$	21	14	1.5	290	422	477
-H	-H	-Br	14	7	2.0	260	340	358



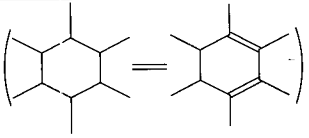
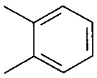
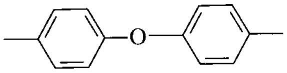
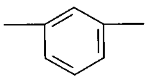
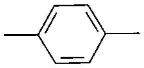
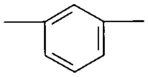
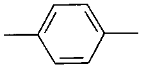
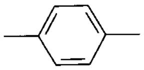
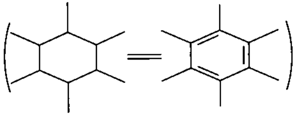
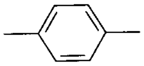
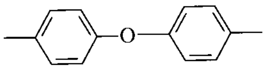
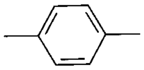
(29)

The polymers attained their maximum intrinsic viscosities (Table 21) in 1–3 h in refluxing α-chloronaphthalene or in 18–24 h in refluxing 1,2,4-trichlorobenzene.

Table 21
Viscosities of polydihydrophthalimides and polyphthalimides with the general formula



[97]

-Ar-	-Ar′-	[η] (DMF, 25°C)
Polydihydrophthalimides		
		0.33
	“	0.41
	“	1.01
		0.45
	“	0.52
Polyphthalimides		
		0.41
		0.12

Polymer obtained from *p*-dimaleimide reached an intrinsic viscosity of 1.01 in 4 h in refluxing 1,2,4-trichlorobenzene, while polyimide based on *o*-dimaleimide attained an intrinsic viscosity of only 0.33 after 24 h under the same conditions. Either there is considerable steric hindrance, which slows the polymerization reaction in the case of the *σ*-isomer, or the series of sharp kinks in the polymer chain limits the root-mean-square end-to-end distance and therefore affects the intrinsic viscosity considerably [96].

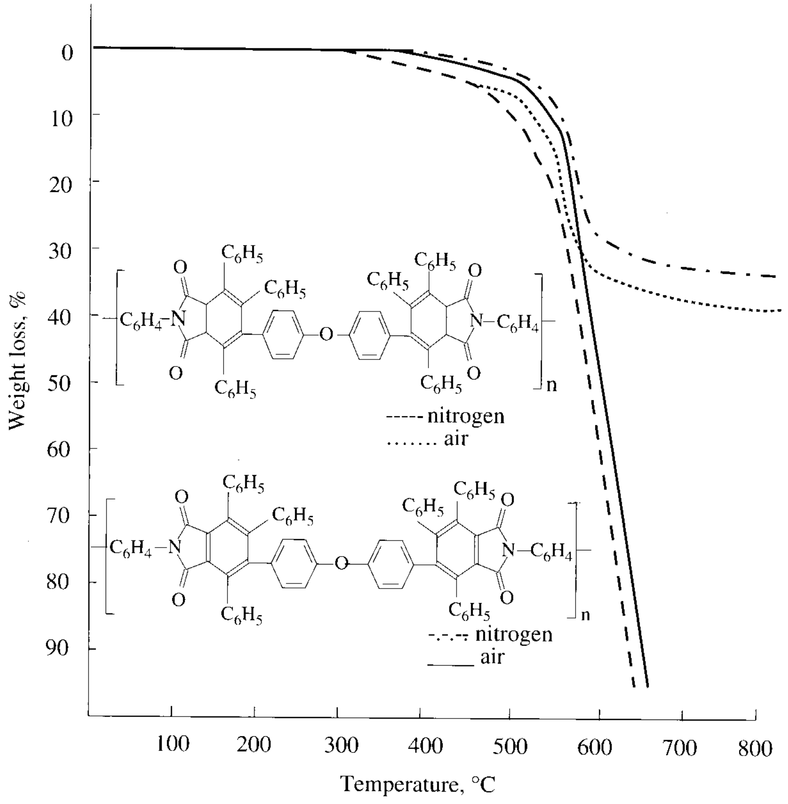
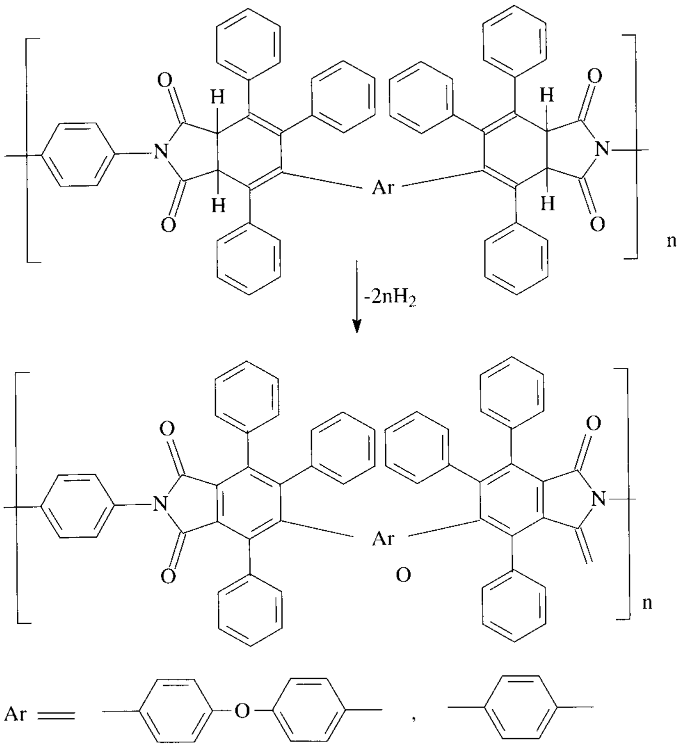


Fig. 5. Thermogravimetric analysis of polydihydrophthalimide and polyimide [97].

The polydihydrophthalimides were soluble in DMF and formed clear, slightly yellow films. Thermogravimetric analysis curves of all the polymers showed an initial break in air near 300 °C followed by gradual weight loss to 530 °C where complete decomposition occurred (Fig. 5) [97]. In a nitrogen or helium atmosphere, after the initial weight loss near 300 °C, the polymer samples lost approximately 30% of their weight near 530 °C and then essentially maintained their weight to 900 °C. The small weight loss near 300 °C can be attributed to dehydrogenation accompanied by slight decomposition.

The polydihydrophthalimides were dehydrogenated by stirring in refluxing nitrobenzene for 12 h to produce aromatic polyphthalimides.



(30)

Dehydrogenation was evidenced by a shift of the high intensity absorption band at 225–235 to 260–270 mμ. Aromatization could also be followed by the disappearance of the singlet peak at 4.34 ppm in the NMR spectra. The conversions to the aromatic polyimides, however, were evidently not quantitative, as the thermogravimetric analysis curves of these polymers still showed a slight weight loss near 300 °C. Heating the polydihydrophthalimides in nitrobenzene also resulted in a sharp decrease in their intrinsic viscosities. The polyphthalimides were obtained in one step when the initial reactions of the appropriate bis-cyclopentadienones and dimaleimides were carried out in refluxing nitrobenzene. The polymers prepared in this manner had nearly identical properties to those obtained by dehydrogenation in nitrobenzene.

Treatment of the polydihydrophthalimides with bromine in 1,2,4-trichlorobenzene resulted in residual bromine in the polymer chain and a decrease in viscosity. Attempts to dehydrohalogenate these polymers were unsuccessful.

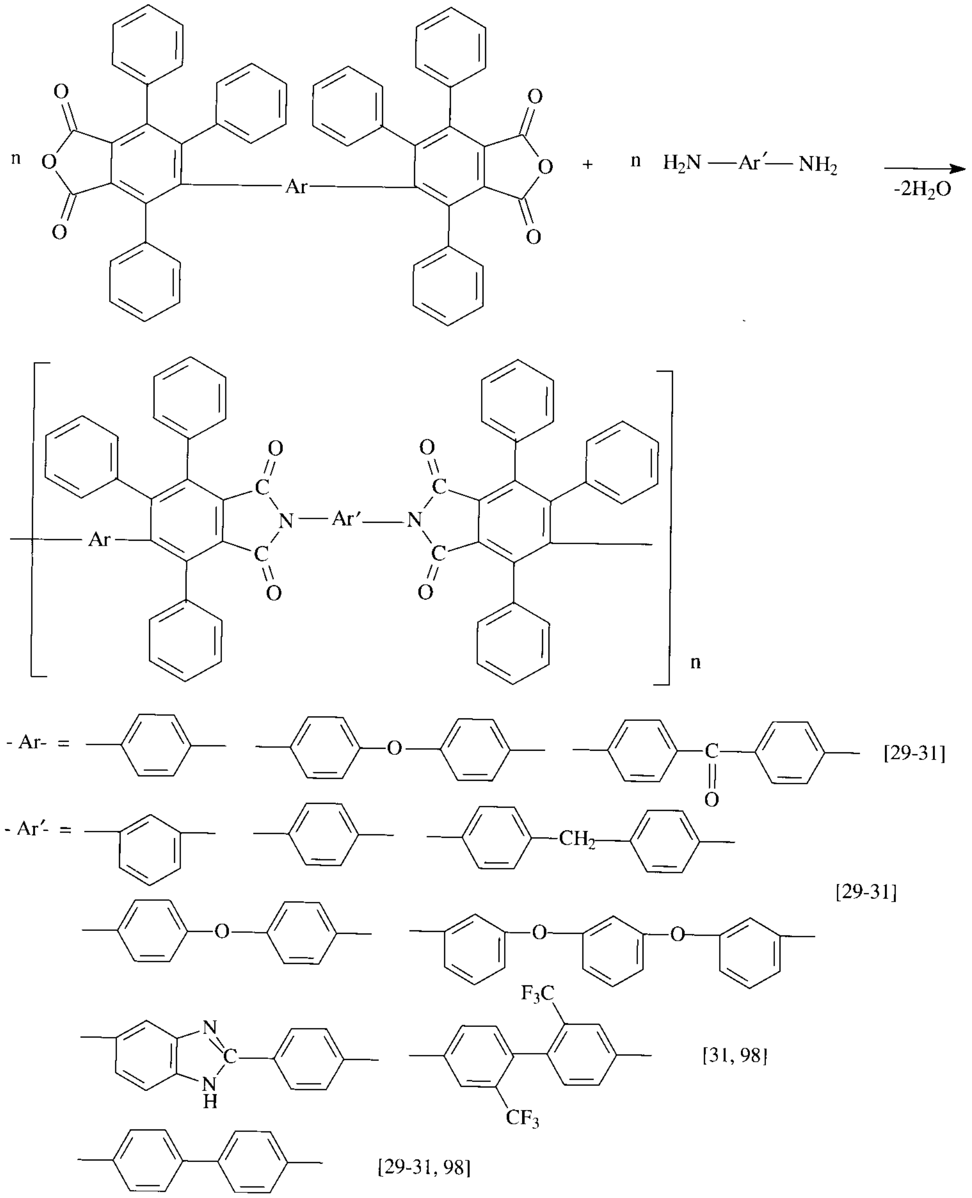
Quantitative dehydrogenation of polydihydrophthalimides was accomplished by heating finely powdered samples in vacuo or in a nitrogen atmosphere to 350 °C. The thermogravimetric analysis curves of the polyphthalimides prepared in this manner showed no weight loss in air until 530 °C, where complete decomposition occurred. In nitrogen the polymers lost approximately 30% of their weight near 550 °C, and then essentially maintained their weight to 900 °C (Fig. 5). These curves are comparable to those obtained for unsubstituted aromatic polypyromellitimides [1]. Thermal dehydrogenation, however, also resulted in a sharp decrease in intrinsic viscosity due to decomposition via the dihydrophthalimide linkage.

The polyphthalimides were soluble in DMF and formed brittle, dark yellow films. Polyimides demonstrating much higher solution viscosities and, correspondingly higher molecular weights were obtained by the reaction of phenylated aromatic tetracarboxylic acids dianhydrides—derivatives of bis-cyclopentadienones—with aromatic diamines [29–31,98].

4.3. Synthesis of phenylated polyphthalimides, polynaphthylimides and polynaphthoylenebenzimidazoles on the basis of highly phenylated bis-(phthalic) and bis-(naphthalic) anhydrides

4.3.1. Synthesis of phenylated polyphthalimides

Reactions were carried out according to the scheme:

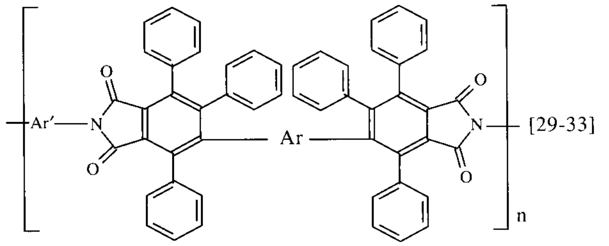


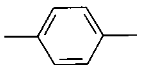
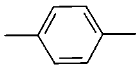
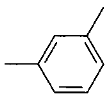
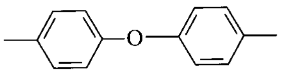
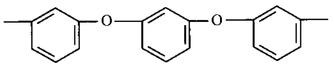
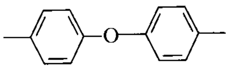
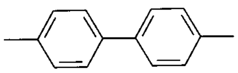
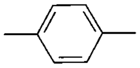
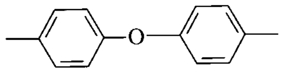
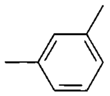
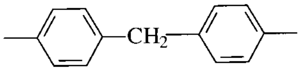
(31)

The phenylated dianhydrides were polymerized with aromatic diamines in DMF or DMAc to obtain the corresponding polyamic acids. The conversion of the polyamic acid precursors to polyimides was then performed chemically via low-temperature cyclodehydration in the presence of dehydration agents and catalysts. The intrinsic viscosities of the polyimides, however, ranged only from 0.4 to 0.6.

The dianhydrides were then polymerized with a series of diamines in *m*-cresol [29–31], using quinoline or benzoic acid [35,98] as catalysts. The diamines used were 2,2-bis(trifloromethyl)benzidine, 2(*p*-aminophenyl)-5(6)aminobenzimidazole and 1,1,1,3,3,3-hexafluro-2,2-bis(*p*-aminophenyl)propane. The polymerization mixtures were stirred at ambient temperature for 1 h and then heated at 202–203 °C for 3 h. Under these

Table 22
Properties of phenylated polyimides with the general formula



<table>
<tr><th rowspan="2">-Ar-</th><th rowspan="2">-Ar′-</th><th rowspan="2">[η]</th><th rowspan="2">T_g^a</th><th colspan="2">$T_{10\%}$</th></tr>
<tr><th>air</th><th>argon</th></tr>
<tr><td></td><td></td><td>0.35</td><td>466</td><td>550</td><td>575</td></tr>
<tr><td>-“-</td><td></td><td>0.86</td><td>416</td><td>545</td><td>557</td></tr>
<tr><td>-“-</td><td></td><td>1.11</td><td>413</td><td>550</td><td>555</td></tr>
<tr><td>“-</td><td></td><td>1.22</td><td>280</td><td>560</td><td>565</td></tr>
<tr><td></td><td></td><td>4.03</td><td>399</td><td>555</td><td>565</td></tr>
<tr><td>-“-</td><td></td><td>0.40</td><td>371</td><td>550</td><td>560</td></tr>
<tr><td>-“-</td><td></td><td>2.80</td><td>360</td><td>545</td><td>550</td></tr>
<tr><td>-“-</td><td></td><td>1.06</td><td>357</td><td>530</td><td>555</td></tr>
<tr><td>-“-</td><td></td><td>1.36</td><td>366</td><td>515</td><td>545</td></tr>
</table>

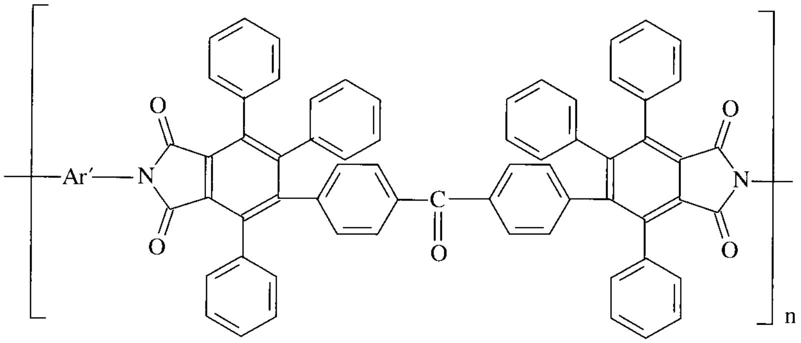
[a] Glass transition temperature as determined by DSC, ΔT – 10°/min

conditions, the intermediate polyamic acids were converted to the corresponding polyimides. The reaction mixtures were added to absolute ethanol to precipitate the white polyimides in nearly quantitative yield. The polymers were then heated under vacuum at 250 °C for 4 h to insure complete imidization.

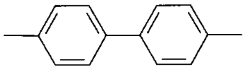
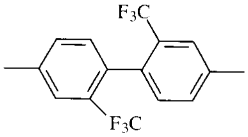
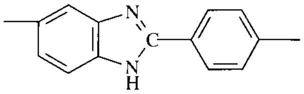
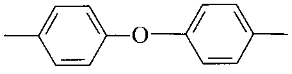
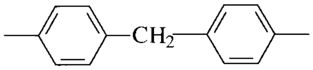
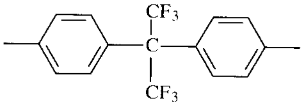
The phenylated polyimides are soluble in *m*-cresol, THF, DMF, DMSO; on heating they are soluble in toluene and pyridine. They have intrinsic viscosities as high as 4.0 dl/g (Table 22, 23). Films cast from chloroform are slightly yellow, transparent and highly flexible.

The glass transition temperatures of the polymers were determined by thermomechanical analysis. The incorporation of the flexible ether linkage in the dianhydride monomer resulted in a lower polymer T_g than the

Table 23
Properties of the phenylated polyimides with the general formula

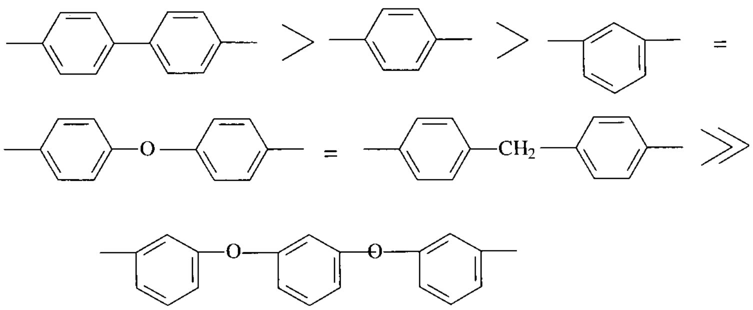


[98]

-Ar-	T_g[a]	$T_{10\%}$		Film properties (25°C)	
		air	argon	σ, MPa	ε, %
	390	600	665	84.3	7.5
	395	610	665	86.6	8.0
	365	625	675	85.4	3.6
	385	605	655	81.9	7.0
	360	580	645	78.3	
	345	565	610	78.3	
	350	575	610	68.0	

[a] Glass transition temperature as determined by DSC, ΔT– 10°/min

incorporation of the same unit in the diamine. The polymer T_g was progressively lowered as the flexibility of the diamine was increased. Essentially the same polymer T_g's were obtained with *m*-phenylenediamine, 4,4′-diaminodiphenyl ether and 4,4′-diaminodiphenylmethane so that the ranking of polymer T_g's is



(32)

Thermogravimetric analysis of the phenylated polyimides showed no weight loss in air or nitrogen until near 530 °C. Isothermal aging studies of the polymers showed no weight loss after 72 h in air at 350 °C or in nitrogen at 400 °c. The polymers did undergo decomposition in air at 400 °C (Fig. 6).

Reactions of 4,4′-bis(2,3,6-triphenyl-4,5-dicarboxyphenyl)benzophenone dianhydride with aromatic diamines were carried out in *m*-cresol/benzoic acid at 180 °C for 5 h. All reactions proceeded homogeneously and led to the formation of phenylated polyimides showing reduced viscosities of 0.66–2.25 dl/g. Properties of the polyimides are given in Table 23.

4.3.2. Synthesis of phenylated polynaphthylimides

Highly phenylated bis(naphthalic anhydrides) were used to prepare polynaphthylimides (PNIs) [34–36,99]—polymers with better chemical resistance than polyphthalimides [2,100]. The use of PNIs is limited by their

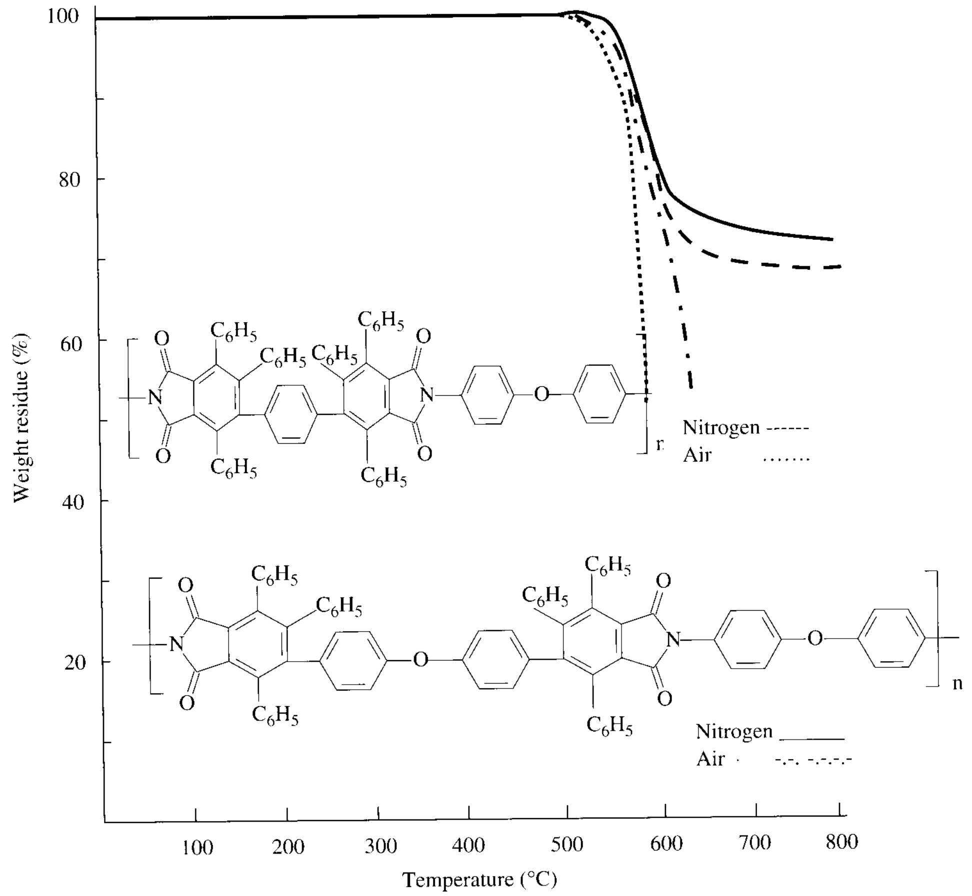
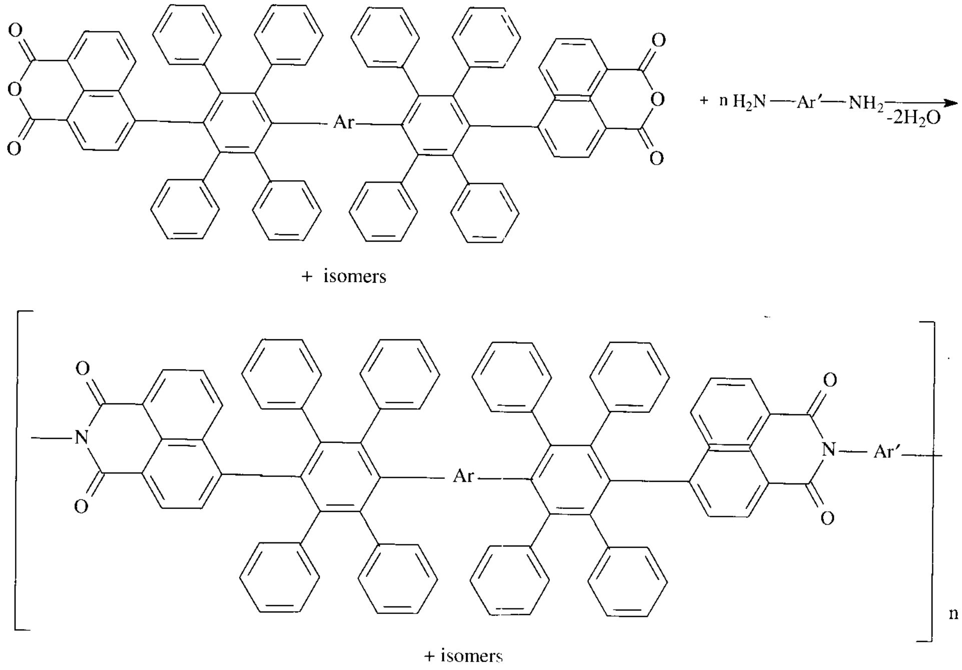


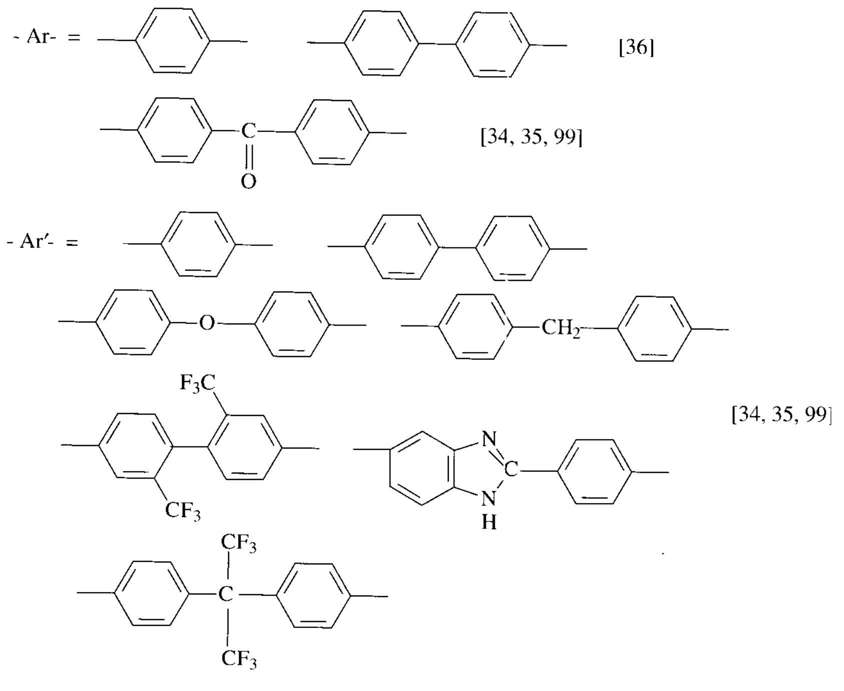
Fig. 6. Thermogravimetric analysis of polyimides (5 °C/min) [32].

poor solubility in the majority of organic solvents and poor processibility. PNIs are usually synthesized by a one-step polycyclocondensation that does not make it possible to synthesize soluble poly(amic acid) prepolymers.

Phenylated PNIs were synthesized by high-temperature polycyclocondensation via the reaction of phenylated bis(naphthalic anhydrides) with equimolar amounts of various diamines according to the scheme:



(33)



(34)

All the above reactions were carried out in phenolic solvents using benzoic acid and benzimidazole as catalysts. All reactions processed homogeneously leading to PNIs with reduced viscosities of 0.52–0.78 dl/g.

X-ray diffractograms demonstrate that the synthesized phenylated PNIs are fully amorphous; probably, this is responsible for their improved solubility: all the tested polymers are soluble in aprotic solvents (NMP, DMF, DMAA, DMSO), as well as in *m*-cresol; when heated, they show solubility in chloroform and toluene.

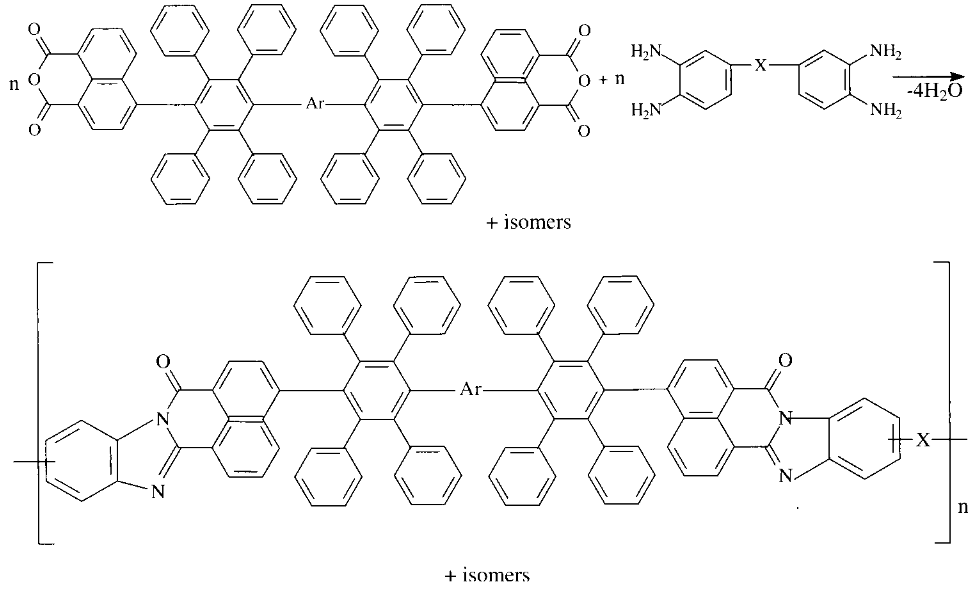
The solubility of the polymers depends on the structure of the aromatic diamines used. Polymers containing ether, methylene, hexfluoroisopropylidene and bulky trifluoromethyl groups rapidly dissolve in organic solvents and have better solubility than phenylated polynaphthylimides with more rigid chains. Benzimidazole-containing polymer is insoluble in chloroform and toluene, possibly because of the rigid, polar benzimidazole groups, which strongly enhance intermolecular dipole–dipole interaction. Finally, the phenylated PNIs are appreciably more soluble than the polynaphthylimides based on 1,4,5,8-naphthalenetetracarboxylic dianhydride [100]. The significant increase in solubility is explained by the presence of various isomeric structures and of many phenyl substituents.

Phenylated PNIs have glass transition temperatures ranging from 340 to 398 °C (Table 24). As might be expected, a higher glass transition temperature is observed for the rigid-chain phenylated PNIs containing *p*-diphenylene and benzimidazole moieties. Contrary to expectations, polymers bearing *p*-phenylene moieties exhibits a lower T_g than the above-mentioned polymers; this seems to be due to the large number of phenyl side groups per phenylene backbone group.

Phenylated PNIs possess excellent thermal stability (Table 24). According to dynamic TGA, temperatures corresponding to the 10% weight loss of phenylated PNIs in air and argon are within 583–614 and 626–680 °C, respectively.

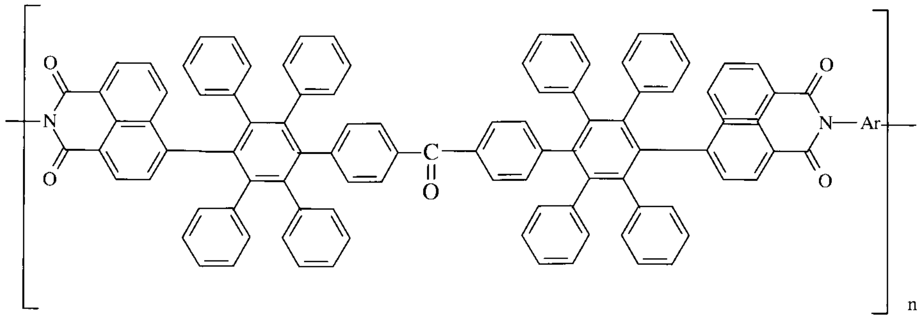
4.3.3. *Synthesis of phenylated polynaphthoylenebenzimidazoles*

Along with phenylated PNIs based on phenylated bis(naphthalic anhydrides), there have been developed phenylated polynaphthoylenebenzimidazoles [34–36,101], combining outstanding thermal, chemical and radiation resistance [2,28]. They were prepared using high-temperature solution polycondensation in phenolic solvents; benzoic acid and benzimidazole were used as catalysts. Reactions of phenylated bis(naphthalic anhydrides) and bis(o-phenylenediamines) were carried out according to the scheme:

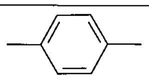
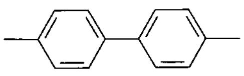
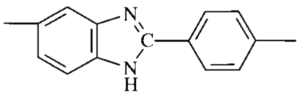
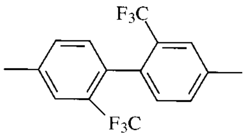
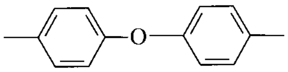
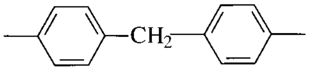
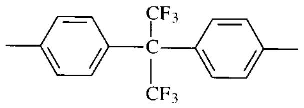


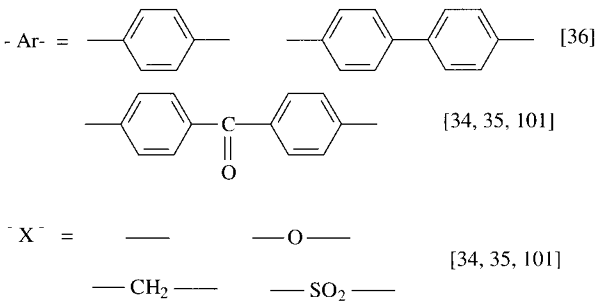
(35)

Table 24
Properties of the phenylated polynaphthylimides with the general formula



[37-39, 99]

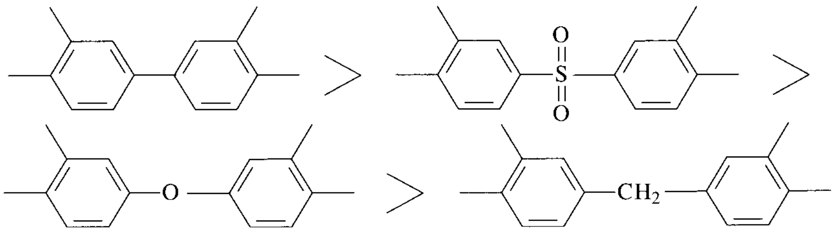
-Ar-	η_{red} (DMF, 25°C) dl/g	Film properties		T_g, °C	$T_{10\%}$ (TGA) ΔT = 10°/min, air/Ar
		σ, MPa	ε, %		
	0.76	79.5	6.0	375	615/680
	0.71	83.0	3.0	400	590/660
	0.62	66.1	6.0	390	615/630
	0.52	82.0	9.0	385	605/660
	0.78	69.0	4.0	370	590/670
	0.71	70.0	8.0	340	580/645
	0.73	65.0	4.5	380	595/625



(36)

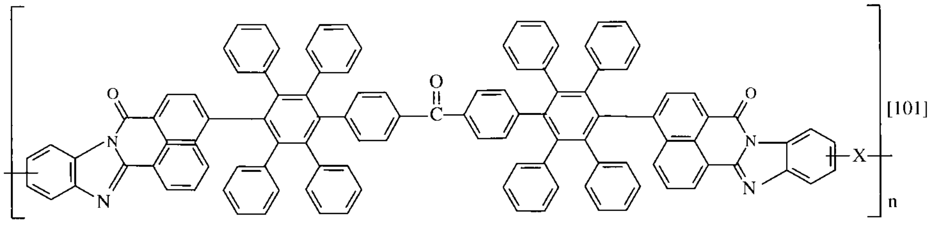
All polymerization reactions proceeded homogeneously and led to the formation of polynaphthoylenebenzimidazoles soluble in NMP, DMF, DMAc, DMSO, *m*-cresol, THF and chloroform; η_{red} of polymer solutions in NMP ranged between 0.69 and 0.91 dl/g (Table 25).

The thermal behavior of polymers was studied by TMA and TGA (Table 25). For the majority of polymers, the softening temperatures were in the 380–426 °C range and, depending on the naure of the tetramine component, decreased, the sequence:



(37)

Table 25
Properties of phenylated polynaphthoylenebenzimidazoles with the general formula



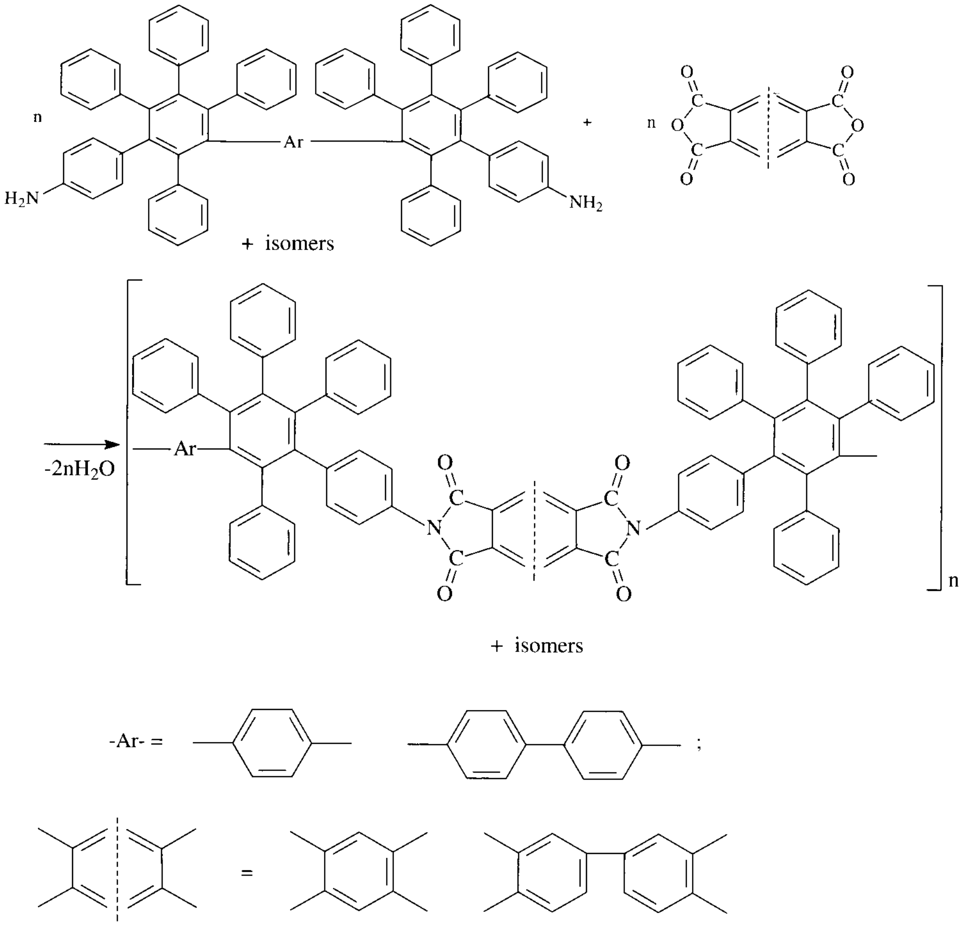
-Ar-	η_{reg}, (NMP, 25°C) dl/g	M_w	T_g, °C	$T_{10\%\ (TGA)}$, air/argon	Film properties (25°C)	
					σ, MPa	ε, %
-	0.80	378,100	425	620/680	68.8	5.5
-O-	0.72	560,000	390	590/660	61.7	5.0
-CH$_2$-	0.91	157,800	380	550/670	62.4	4.8
-SO$_2$-	0.69	141,200	400	600/660	61.0	4.5

According to dynamic TGA, the polymers have excellent thermal stability. Temperatures corresponding to the 10% weight loss in air and argon are within 660–680 and 552–623 °C, respectively. The incorporation of flexible linkages somewhat lowers the thermal stability of the polymers tested (Table 25).

All polymers produced films. The tensile strength of these films ranges from 61.0 to 68.8 MPa; the elastic modulus is between 2.00 and 2.25 GPa; and elongation at break is in the range from 4.5% to 5.5% (Table 25).

4.4. Synthesis of phenylated polyphthalimides and polynaphthylimides based on highly phenylated aromatic diamines

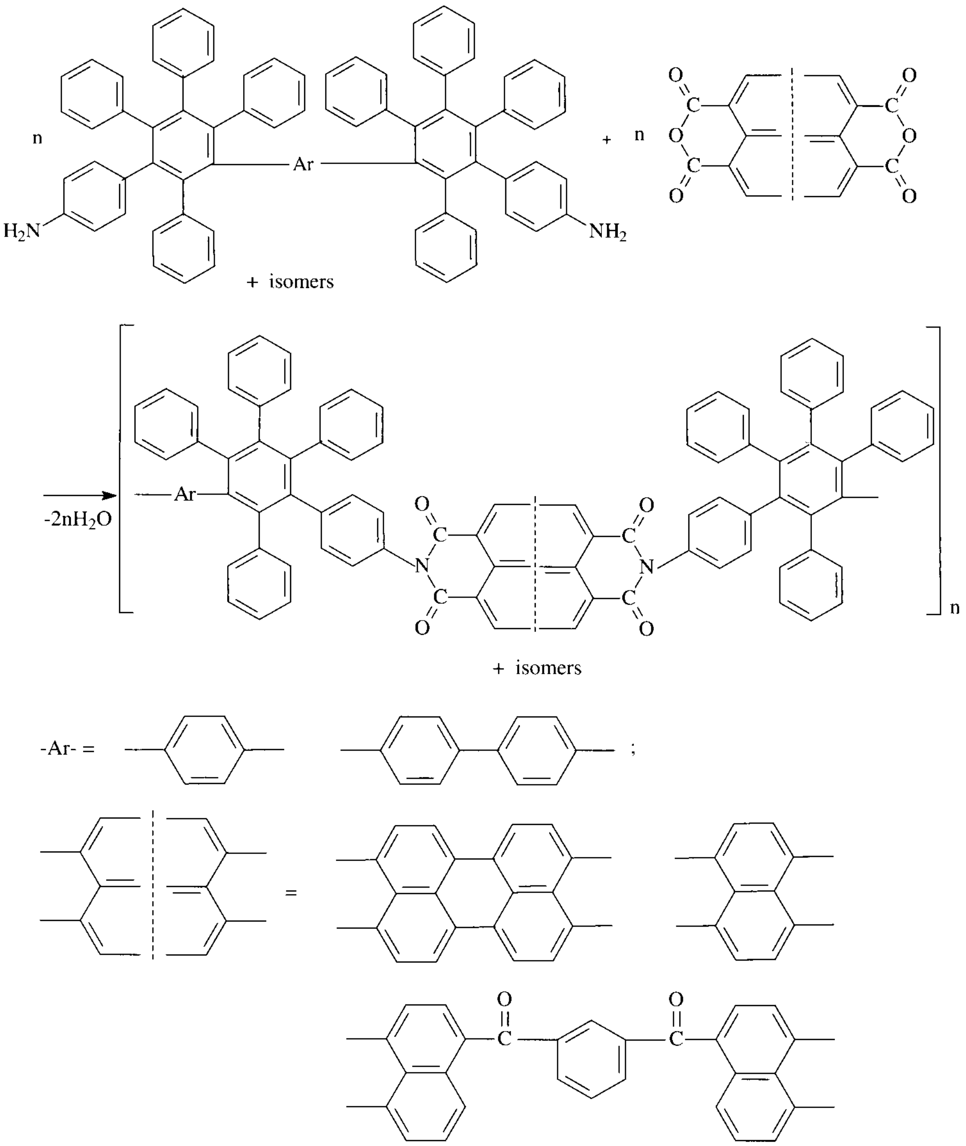
Highly phenylated aromatic diamines prepared in accordance with Ref. [37] were reacted with aromatic tetracarboxylic acid dianhydrides free of "bridging" groups—dianhydrides of pyromellitic and diphenyl-3,3'4,4'-tetracarboxylic acids [37]:



(38)

Reactions were carried out under conditions of high-temperature solution polycyclocondensation using *m*-cresol as the solvent and benzoic acid/benzimidazole as the catalyst [37]. All reactions proceeded homogeneously and led to the formation of high molecular weight ($\eta_{\text{red, NMP}} = 1.1$–$2.8$ dl/g) polyphthalimides soluble in a wide variety of organic solvents, including NMP, THF, $CHCl_3$, etc. Transparent films were cast from solutions in $CHCl_3$. Glass transition temperatures of the polymers prepared ranged between 400 and 450 °C; their degradation temperatures by DTGA (10% weight loss in air, $\Delta T = 4{,}5\,°\text{C/min}$) were 540–560 °C [37].

Reaction of the above-mentioned highly phenylated diamines with the six-membered dianhydrides—perylene-3,4,9,10-tetracarboxylic, naphthalene-1,4,5,8-tetracarboxylic and isophthaloyl-bis(naphthalic) acid derivatives—led to the formation of polymers containing six-membered naphthylimide rings in the main chains [102]:



(39)

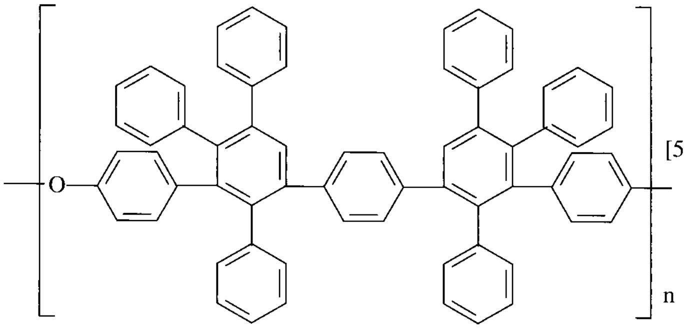
All reactions were carried out in boiling *m*-cresol using benzoic acid and benzimidazole as catalysts. Polynaphthylimides and polyperyleneimides thus obtained combined good solubility in organic solvents and film-forming properties with high glass transition temperatures and high degradation temperatures [102].

5. Applications

The combination of high molecular weights and solubility in organic solvents make phenylated polyphenylenes good candidates for thermostable films. However, when the film of phenylated polyphenylene was cast from benzene material was somewhat brittle [58] (Table 26).

The electrical properties of this polymer from 23 to 280 °c and from 100 to 100,000 Hz are quite interesting, particularly because of the retention of low dielectric loss factors to very high temperature (Fig. 7). The dielectric constants are nearly flat versus frequency at any given temperature and change relatively slowly with increasing temperature at constant frequency. Thus this polymer is a good insulator at room temperature [55].

Table 26
Mechanical properties of phenylated polyphenylene film



[55]

Film thickness	Tensile strength	Elongation	Tensile modulus
0.94 mils	10.1 kpsi	6.22%	277.2 kpsi

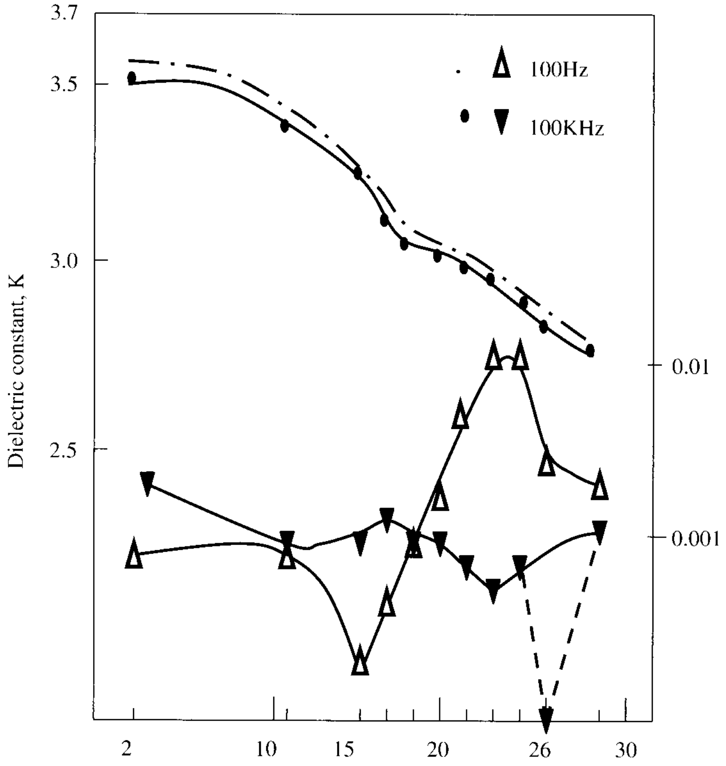
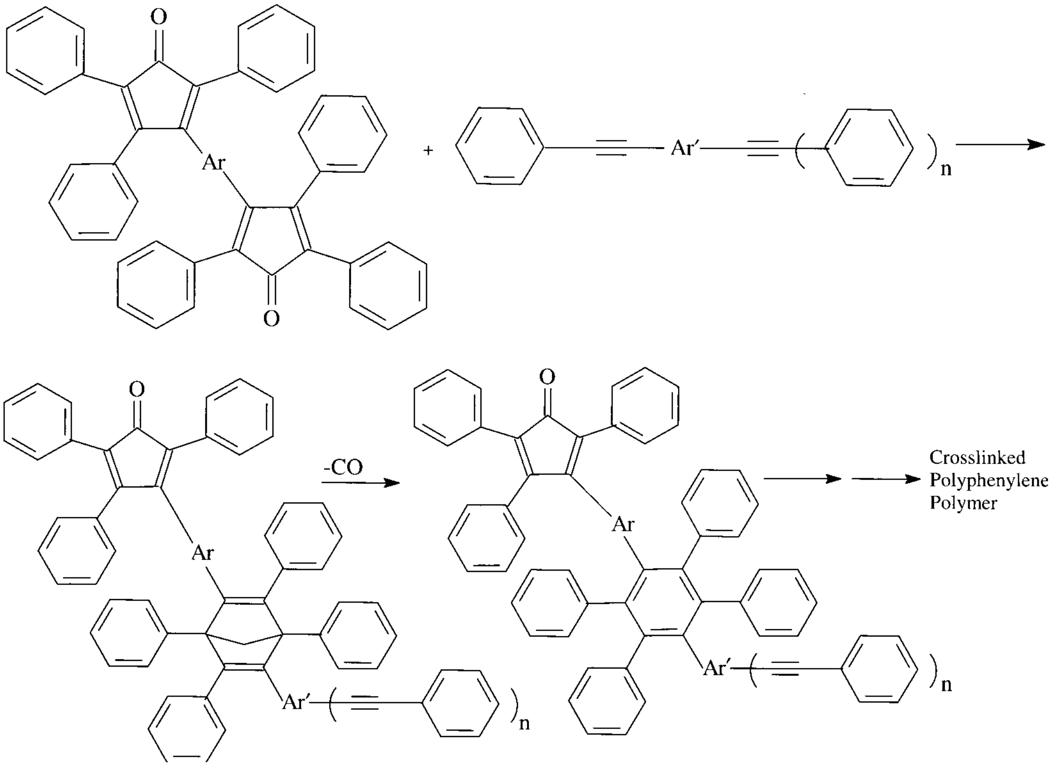


Fig. 7. Dielectric constants of phenyl substituted polyphenylenes [55].

Dielectric measurements showed that phenylated polyphenylenes have lower dielectric constants (2.65–3.00 at 0% humidity) [91] than typical polyimides (3.0–3.5) [103,104]. Apparently, this effect can be explained by high free volume and the absence of polar groups in the polymer chain. At 50% relative humidity, ε' values of the polymers increases by only 2%, whereas for polyimides and polyarylethers, values reach ca.10–20% [103,104]. Possibly, this is related to higher hydrophobicity of PSPPs compared to polyimides and polyarylethers. Polymer containing a hexafluoroisopropylidene group shows a rather low value of ε' (2.65 at 0% humidity) that remains almost unchanged when the humidity in increased to 50% ($\varepsilon' = 2.66$). The introduction of a bulky hexafluoroisopropylidene group into a polymer chain increases the free volume and hydrophobicity of the polymer, and decreases its packing density and electron polarizability. The hydrophobicity, the high thermal stability and the low dielectric permeability of PSPPs make these polymers promising as interlayer insulators in the packages of multiintegral schemes.

These materials have recently become of interest as novel organic dielectrics, owing to their high molecular weight, high T_g, thermal/mechanical robustness, high solubility in a variety of organic solvents, ease of application as thin films and polymerization chemistry that is conducive to incorporating organic substituents.

The approach that was commercially implemented as the SILK dielectric involves the synthesis of cross-linked polyphenylenes by the reaction of polyfunctional cyclopentadienone and acetylene-containing materials [105,106].

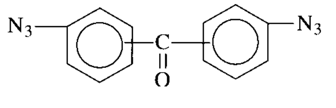


(40)

In the preparation of polyphenylenes from cyclopentadienone and acetylene-containing monomers, the initial oligomers formed are soluble and can thus be processed. Further reaction on a silicon wafer converts the oligomers to cross-linked polymers that have properties suitable for use as interlayer dielectrics.

Methyl-containing PSPPs have been used for the development of dielectrics having low water uptake coupled with photodefinability [24,25]. Addition of the methyl groups was specifically designed to generate sites for cross-linking by photogenerated radicals.

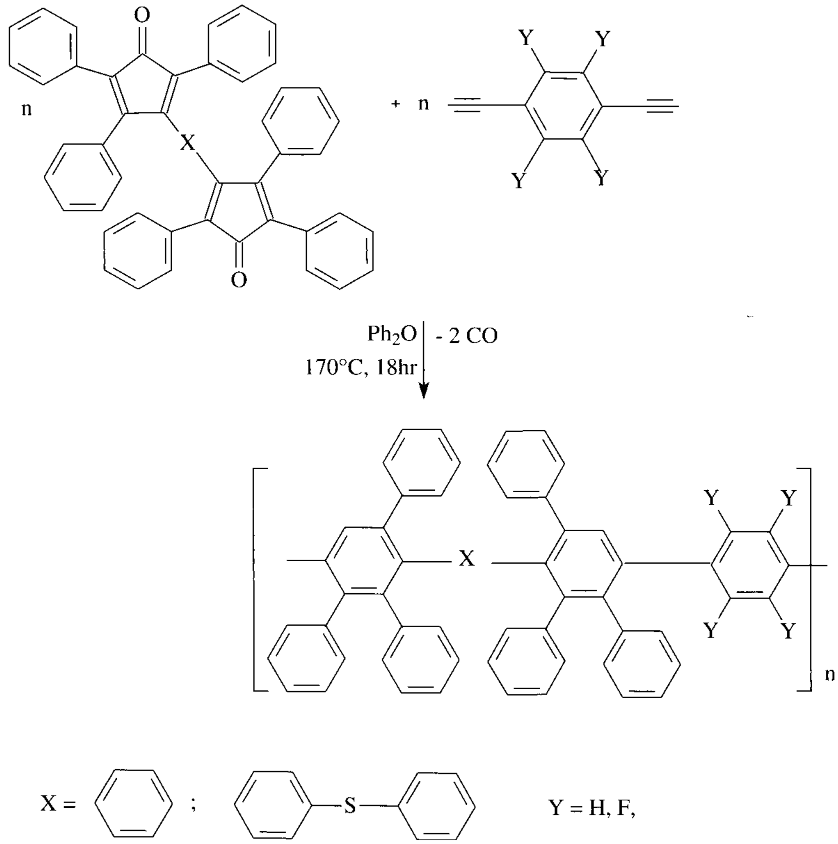
For imaging, photocross-linking agents, such as bis-azides:



(41)

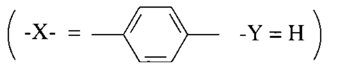
were incorporated into polyphenylene films. Initial imaging studies of polyphenylene films showed that the sensitivity of the system increased with increasing molecular weight of the polyphenylene, while bis-azide concentration was held constant at 10 wt%. The dose needed to pattern methyl-containing PSPP was approximately 150 mJ/cm^2. Increasing the number of methyl groups resulted in higher sensitivities.

PSPPs are attractive candidates for gas-separation membranes [107]. Because of steric interactions, the phenyl rings tend to orient orthogonally, which prevents ring conjugation. These steric interactions result in increased polymer free volume, which directly affects gas permeability [108], and reduced segmental mobility, which results in greater selectivity. PSPPs for gas-separating membranes were prepared according to the scheme:



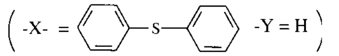
(42)

Owing to the high solubility of these materials in organic solvents, thin films were easily prepared from toluene by spin coating onto a mesoporous alumina support, dried and loaded into a gas permeation instrument. The membranes were tested for gas permeabilities with oxygen, nitrogen, methane, hydrogen, carbon dioxide and helium. The parent polymer, containing



(43)

displayed selectivities (all permeabilities in Barrer units) O_2:N_2 = 4.1:1 with $P_{O2} = 1.9$ and $P_{N2} = 0.47$. Introducing a bend or kink through a heteroatom such as sulfur, may result in reducing the packing density of the polymer and increasing internal free volume. As a result, permeation measurements for the polymer with



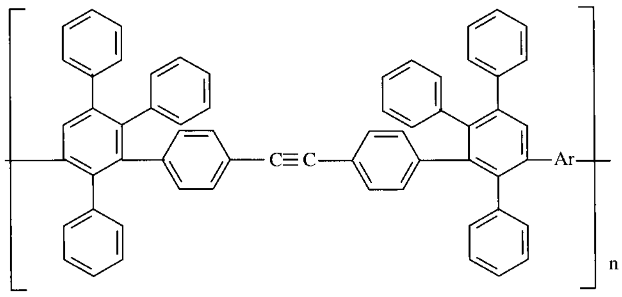
(44)

revealed lower O_2:N_2 selectivity (1.1:1) than was observed for parent polymer but higher permabilities ($P_{O2} = 2$ and P_{N2} of 7.2). The introduction of fluorine groups onto the backbone phenylene resulted in measured permeation rates for oxygen (200) and nitrogen (60).

One additional area of potential applications of PSPPs is photoluminescent and electroluminescent materials.

Photophysical properties of acetylene-containing PSPPs were investigated by absorption and fluorescence spectroscopy. The absorption and fluorescence properties of different acetylene-containing PSPPs are given in

Table 27
Absorption (λ_a) and fluorescence (λ_f) spectra of polyphenyleneethynylenes



[20, 82]

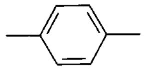
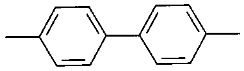
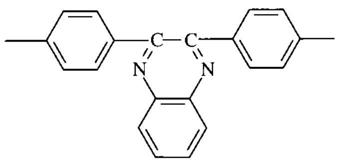
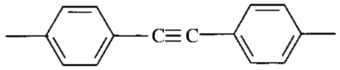
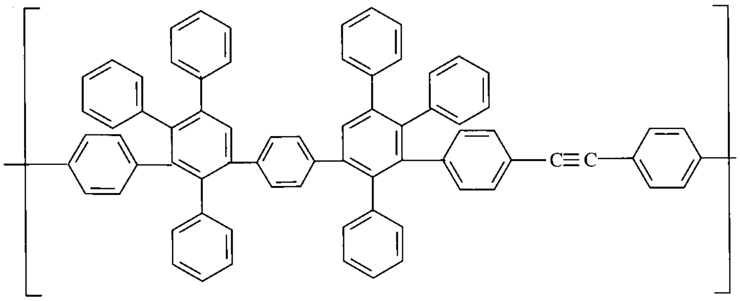
-Ar-	λ_a (nm)	λ_f (nm)
	435	548
	420	531
	426	540
	440	580
	438	562

Table 27. As may be seen from the table, absorption maxima of PSPPs are in the range $\lambda_a = 420$–$440\,\text{nm}$, corresponding to the π–π^* transition in conjugated polymeric systems [20].

Some of PSPPs are fluorescent materials. The fluorescence maximum λ_c for polymer containing 2 acetylenic groups per repeat unit is shifted towards the long-wavelength region when compared with other acetylene-containing PSPPs; this is probably due to an increase in conjugation in this polymer. On other hand, λ_f for polymer is shifted towards the red region as compared with other PSPPs; this is probably due to an increase of conjugation: for example, an increase of the concentration of ethynylic groups per polymer unit [20].

Polynaphthoylenebenzimidazoles based on highly phenylated bis(naphthalic anhydrides) also demonstrate photo- and electroluminescent activity [36]. Absorption, fluorescence and electroluminescence spectra are given in Figs. 8 and 9 [36].

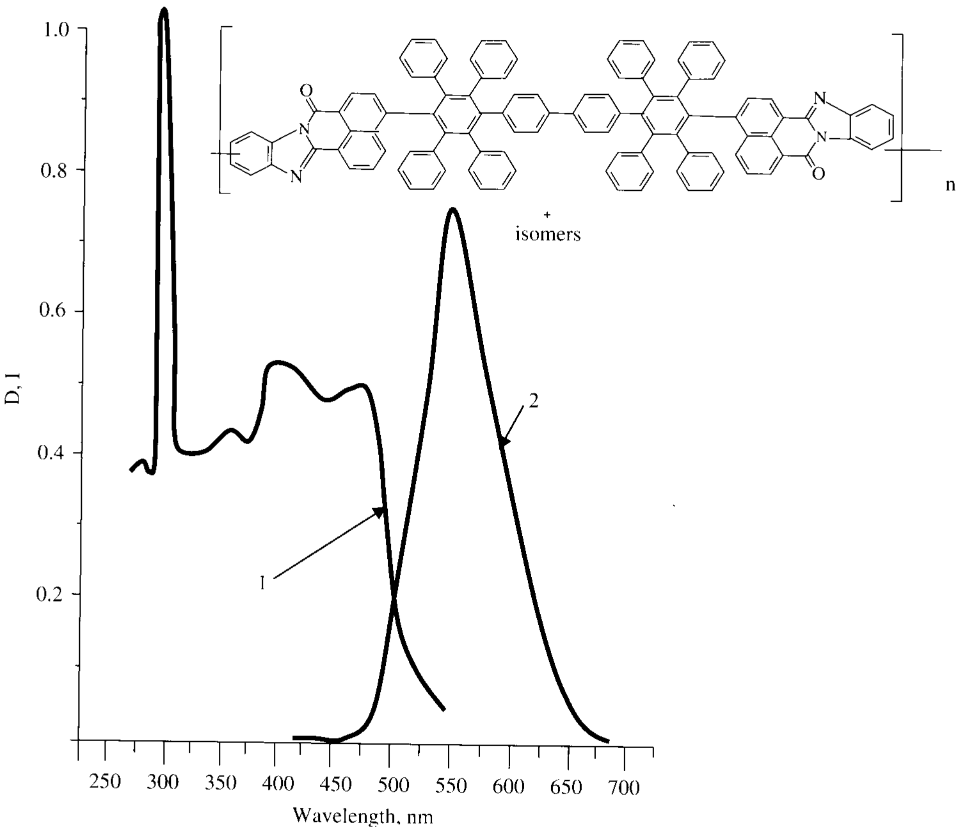


Fig. 8. Absorption (1) and fluorescence (2) spectra of the phenylated polynaphthoylenebenzimidazole [36].

6. Conclusions

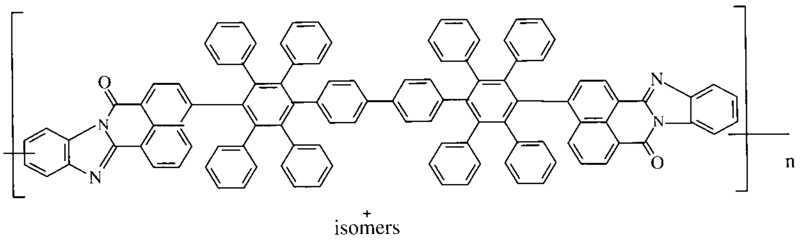
Highly arylated bis-cyclopentadienones containing aromatic carbocyclic, heterocyclic and aliphatic connecting groups were synthesized by the reaction of the corresponding bis-benzyls with twofold molar amounts of unsubstituted or substituted 1,3-diphenylacetones. Reaction of bis-cyclopentadienones thus obtained with maleic anhydride followed by aromatization of reaction products and with 4(phenylethynyl)naphthalic anhydride resulted in new families of highly phenylated bis(phthalic) and bis(naphthalic) anhydrides.

Diels-Alder polyaddition of arylated bis-cyclopentadienones to various diethynylarylenes and di(arylethynyl)arylenes resulted in highly phenylated polyphenylenes demonstrating unique combinations of outstanding solubility in common organic solvents with high molecular weight, film-forming properties and very high thermal stability.

Diels-Alder polyaddition of phenylated bis-cyclopentadienones to bis-maleimides resulted in high molecular weight organosoluble polydihydrophthalimides, which were converted to the corresponding highly phenylated polyphthalimides. High molecular weight organosoluble phenylated polyphthalimides were also prepared by the reaction of highly phenylated bis(phthalic)anhydrides with aromatic diamines under conditions of high-temperature solution polycyclocondensation in phenolic solvents.

High molecular weight organosoluble phenylated polynaphthylimides and polynaphthoylenebenzimidazoles were prepared by the reaction of highly phenylated bis(naphthalic)anhydrides with aromatic diamines and bis(*o*-phenylenediamines) under conditions of high-temperature polycyclocondensation in phenolic solvents.

The new polymers developed may find application as low dielectric constant materials for microelectronics, for gas-separation membranes and materials with photoluminescent and electroluminescent activities.



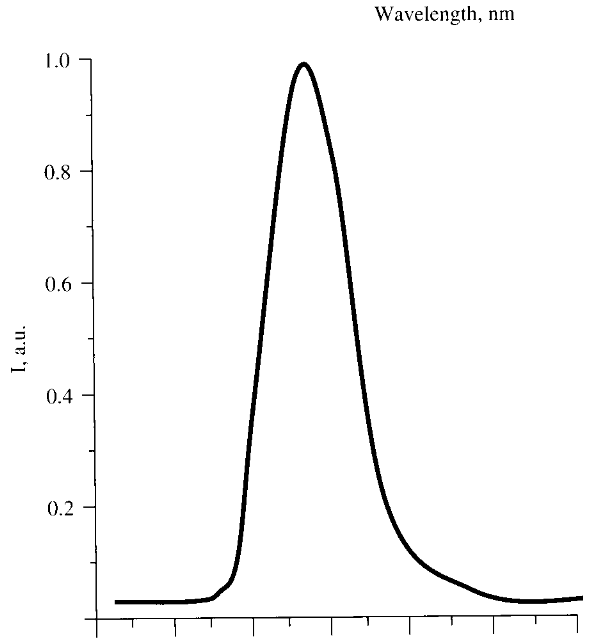


Fig. 9. Electroluminescence spectrum of phenylated polynaphthoylenebenzimidazole.

A very promising potential application of the phenylated polyphenylenes is the production of proton exchange membranes for fuel cells [109] based on the functionalized (sulfonated, phosphorylated) polymers of this class.

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