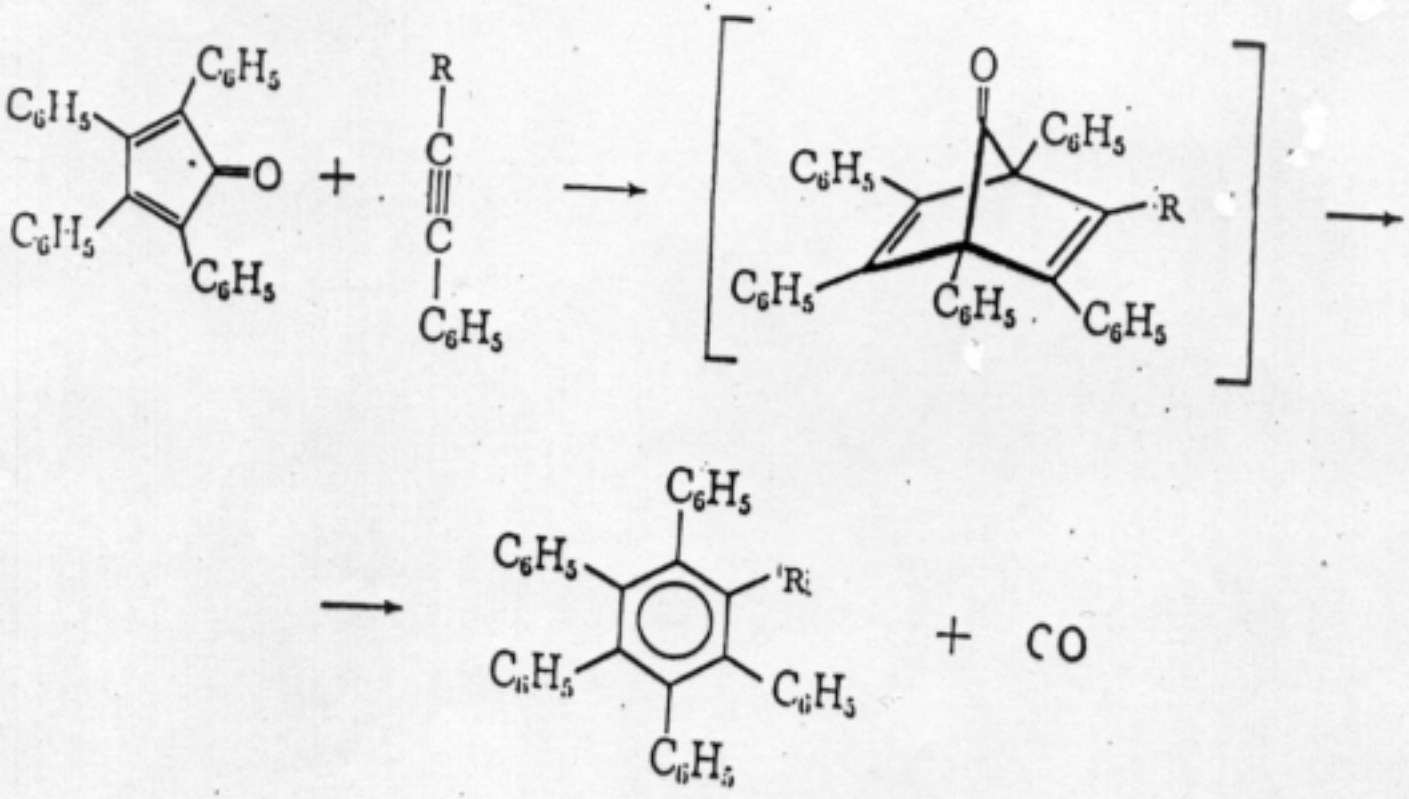
New Aromatic Diels-Alder bis- and polyadducts: new monomers, new polymers.

A.L.Rusanov, M.L.Keshtov.

INEOS RAS.



-R= -H, - C_6H_5

W.Dilthey, G.Hartig. Ber., 67, 2004 (1934)

W.Dilthey, W.Schommer, W.Höschen, H.Dierichs.

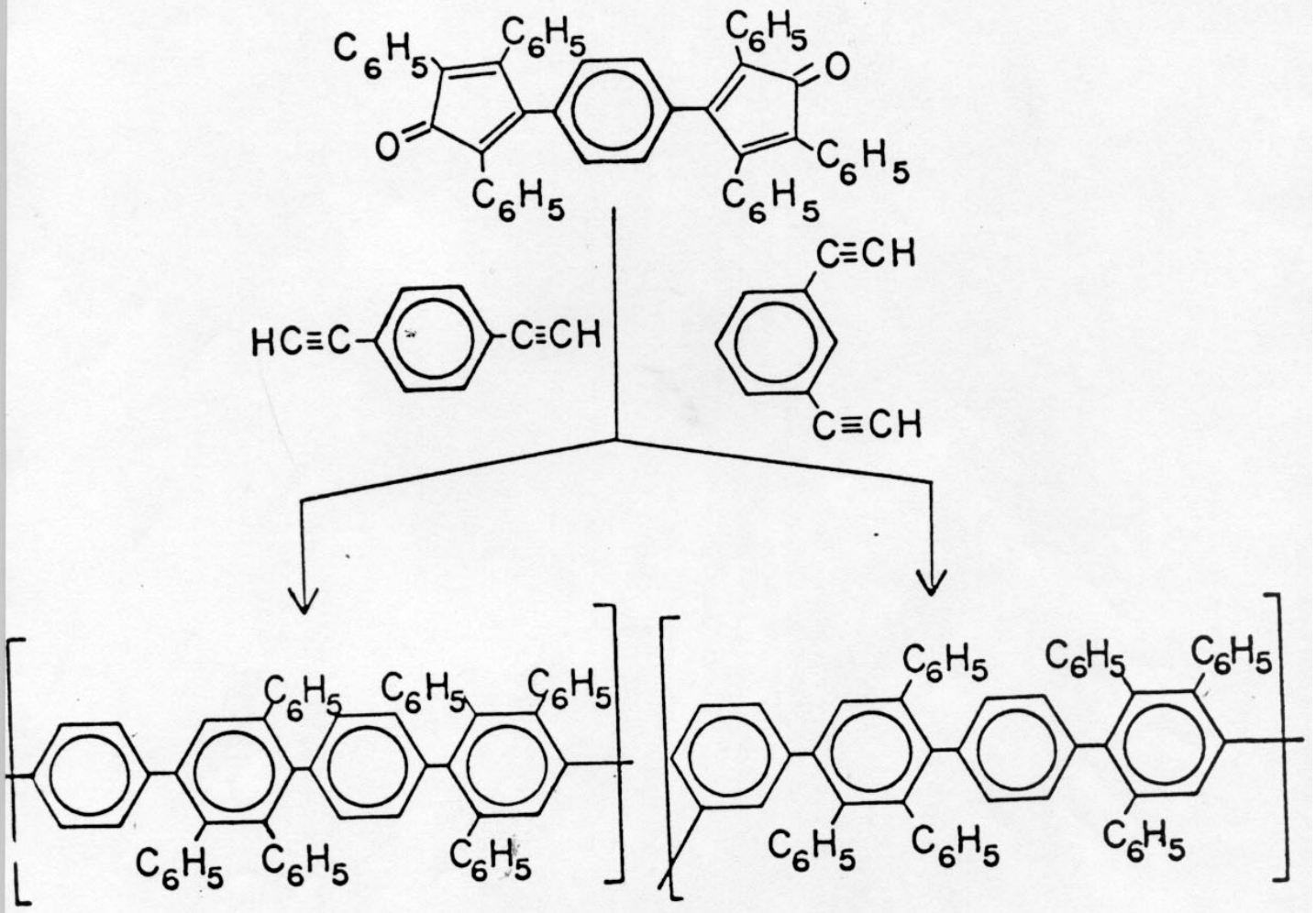
Ber., 68, 1159 (1935)

M.A.Ogliaruso, M.G.Romanelli, E.I.Becker.

Chem. Rev., 65, 261 (1965)

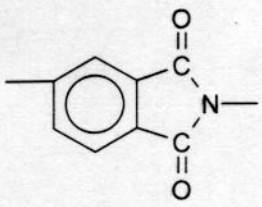
M.A.Ogliaruso, L.A.Shadoff, E.I.Becker.

J.Org.Chem., 28, 2725 (1963)

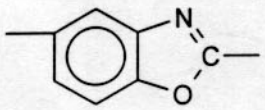


J. K. Stille, F. W. Harris, R. O. Rakutis, and H. Mukamal, J. Polym. Sci. B, 4, 791 (1966).

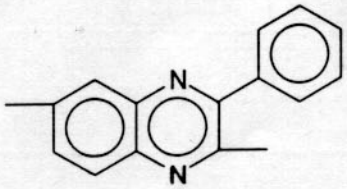
Dielectric constants for different fragments of polymers calculated by Prof. A.A.Askadskiy.



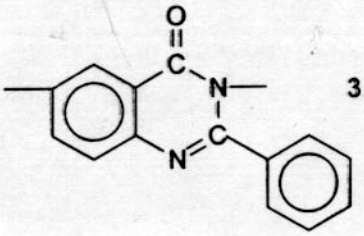
3.57



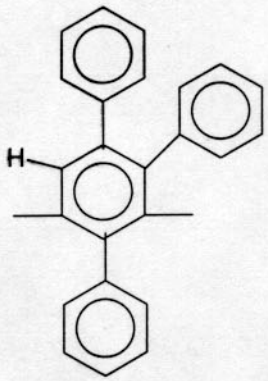
3.97



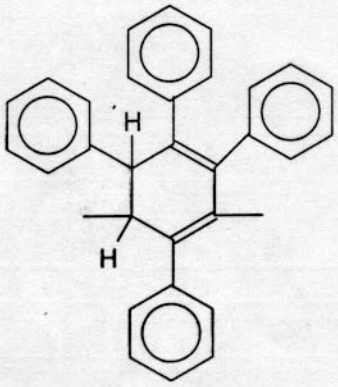
3.59



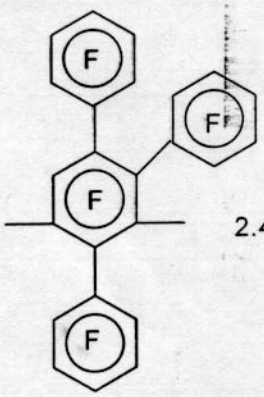
3.35



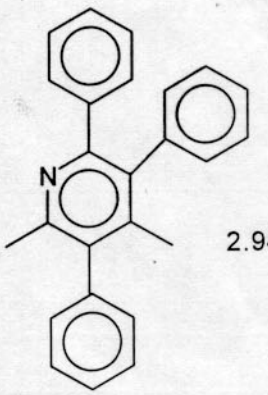
2.69



2.66



2.49



2.94

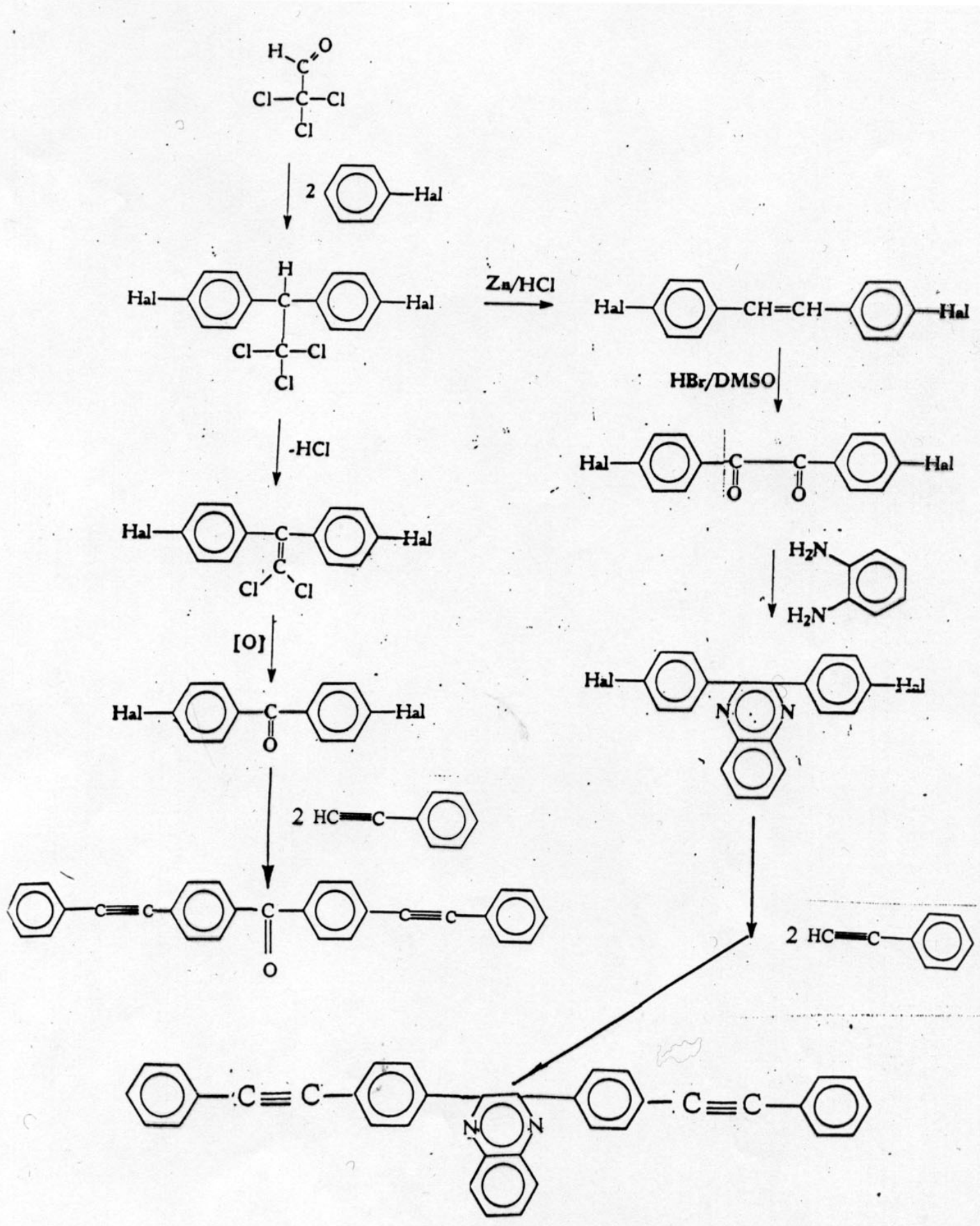
Decreased dielectric constants of phenylated polyphenylenes are due to:

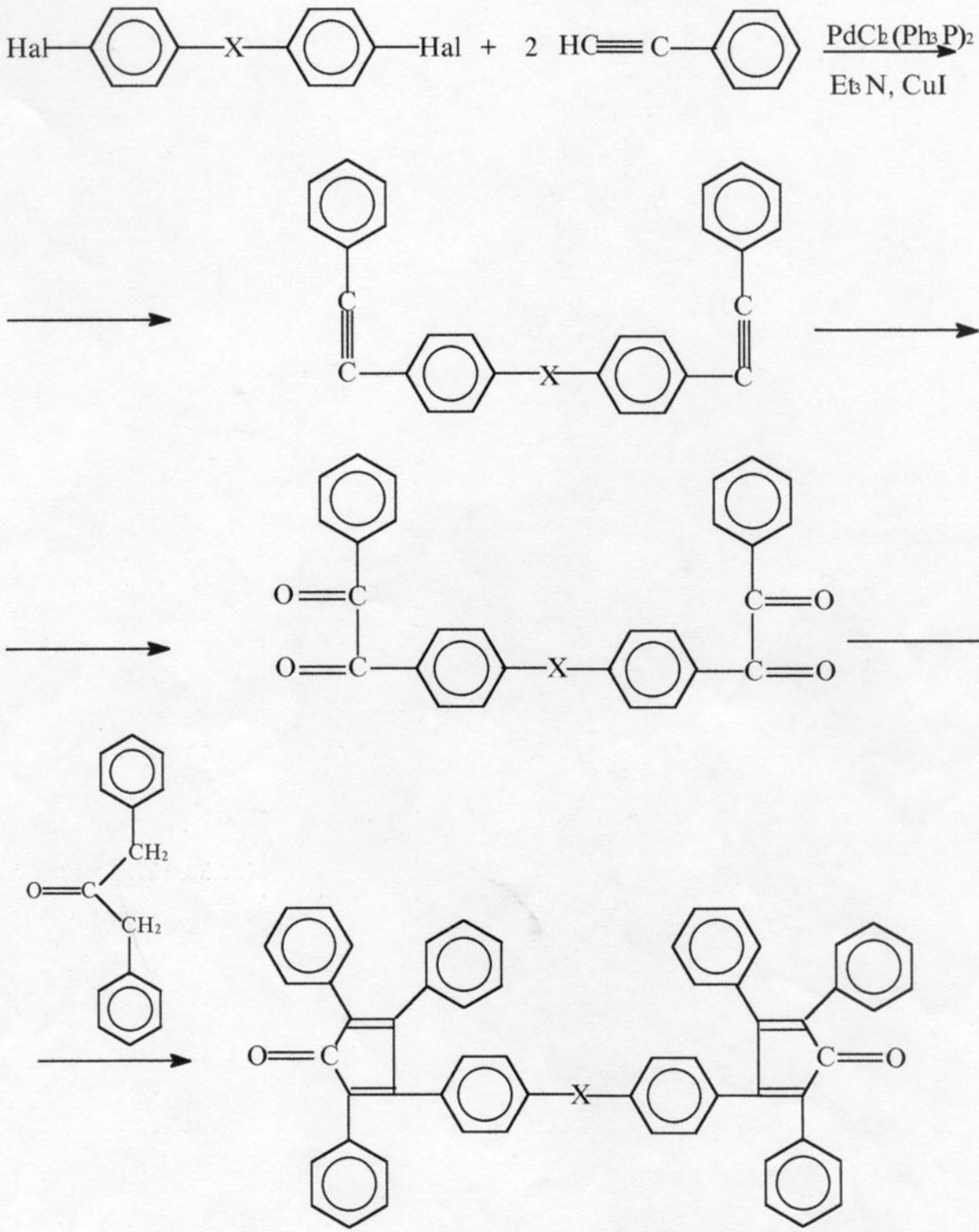
-absence of polar groups;

-large free volume;

-hydrophobisity of the polymers.

Dielectric measurements were performed on 1 ml thick films. The gigahertz dielectric constant measurements were obtained using a Hewlett Packard 8510 Automated Network Analyzer over a frequency range of 8-12 GHz. The films were desiccated overnight prior to measurement and were run at room temperature at 25-35% RH. The reported dielectric constants are quoted at 10GHz and are accurate to ±0.03.


Zn/HCl
HBr/DMSO
-HCl
[O]
2 HC≡C
Hal = Br, I


Hal
X
Hal + 2 HC≡C
PdCl2(Ph3P)2
Et3N, CuI
O
CH2
—X— = —C— (I) , (II) ;
O
N
N

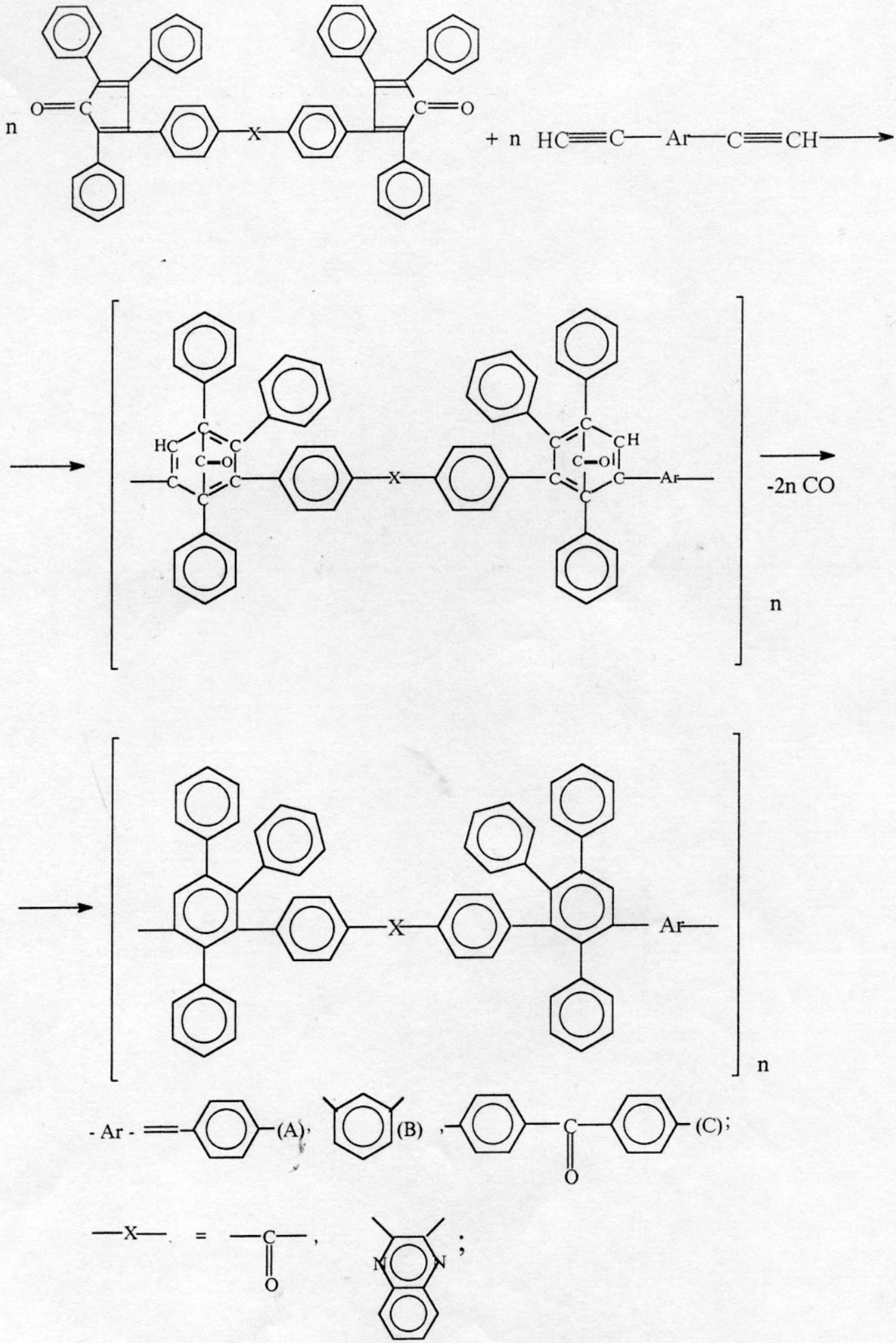
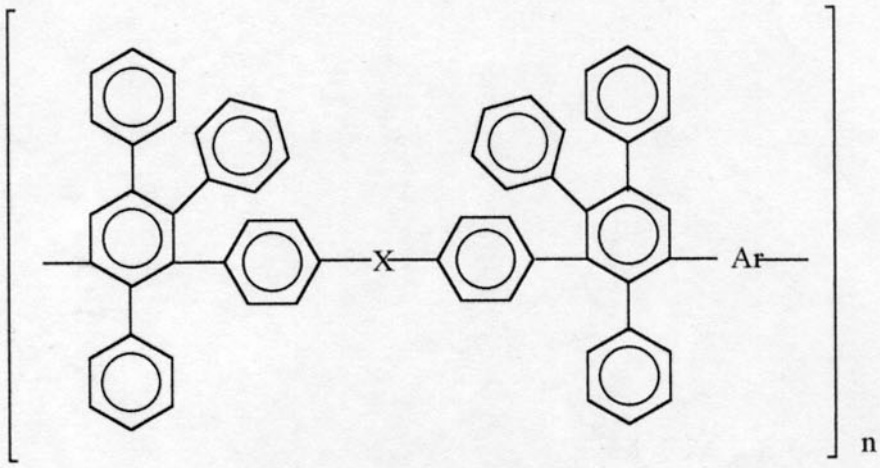

n
+ n HC≡C—Ar—C≡CH
-2n CO
n
n
- Ar -
(A),
(B),
(C);
—X— =
;

Table. Molecular-weight characteristics of the phenylated polyphenylenes of general formula:



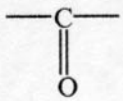
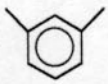
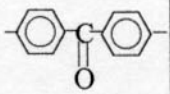
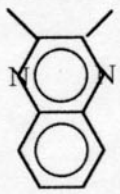
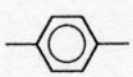
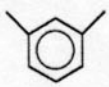
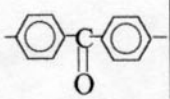
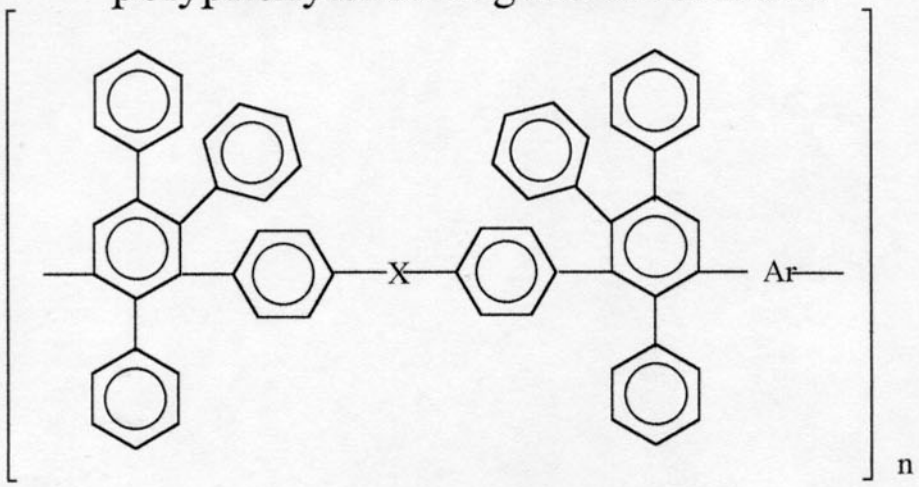
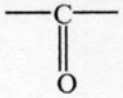
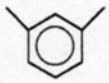
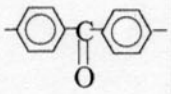
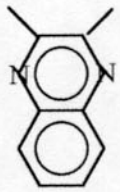
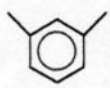
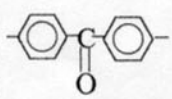
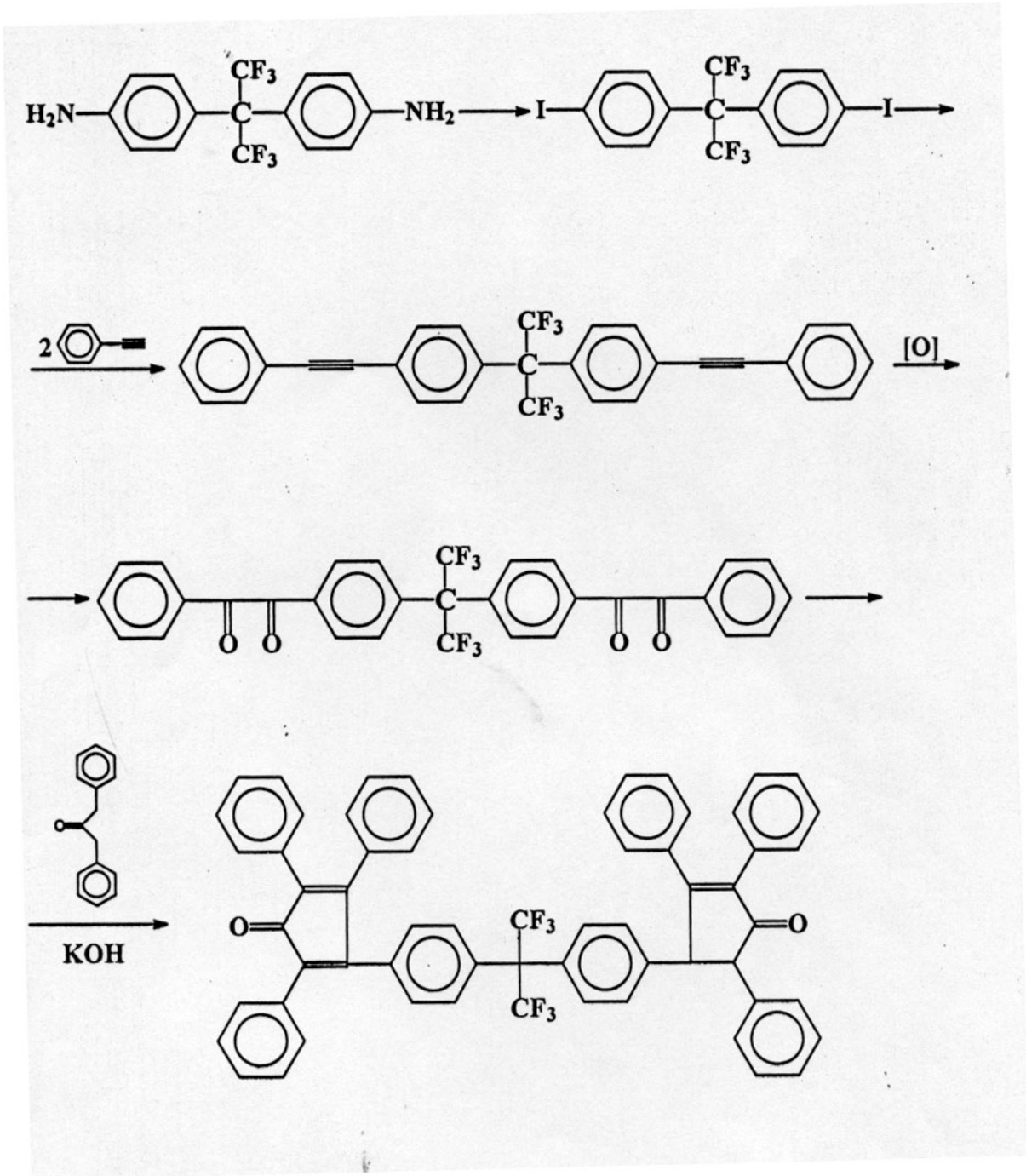
-X-	-Ar-	η red., dl/g	GPC		
			M_n	M_w	M_z
		0.82	59200	207600	480100
«		0.52	27100	78200	145000
«		0.48	48300	258600	310000
		0.19	7300	15600	30500
«		0.18	6400	15300	31500
«		0.29	8800	38400	125300

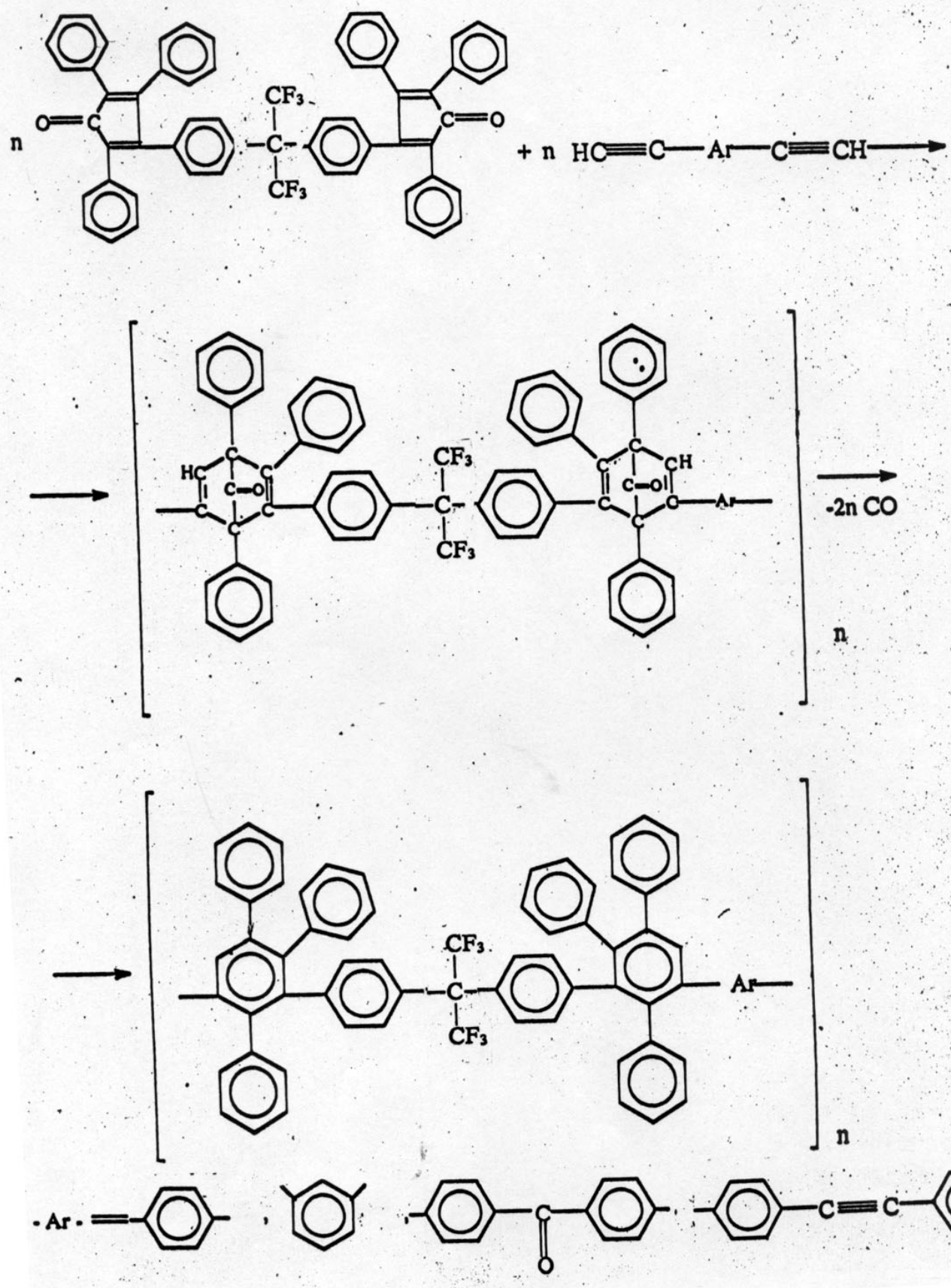
Table. Some properties of chloral-based phenylated polyphenylenes of general formula:



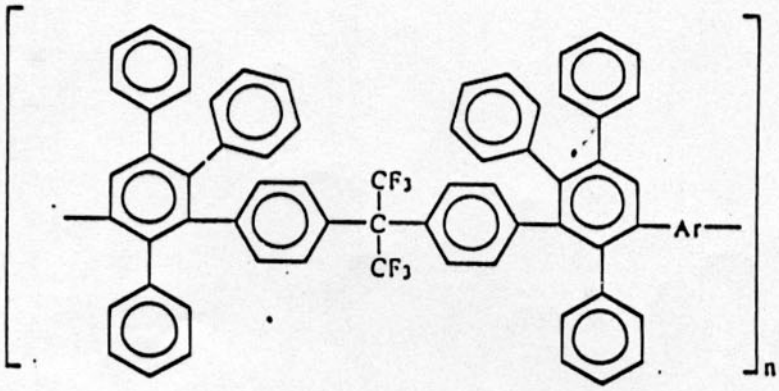
-X-	-Ar-	T_g, °C	$T_{10\%}$,* (TGA, ΔT=4.5 °/min, air), °C		Films properties (25°C)	
					σ, MPa	ε, %
		306	610	(649)	80.4	8.3
«		282	635	(666)	70.7	6.0
«		303	643	(658)	74.2	49
		315	625	(639)	-	-
«		308	628	(650)	-	-
«		301	630	(641)	-	-

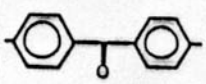
*** —in parentheses are given $T_{10\%}$ in argon.**

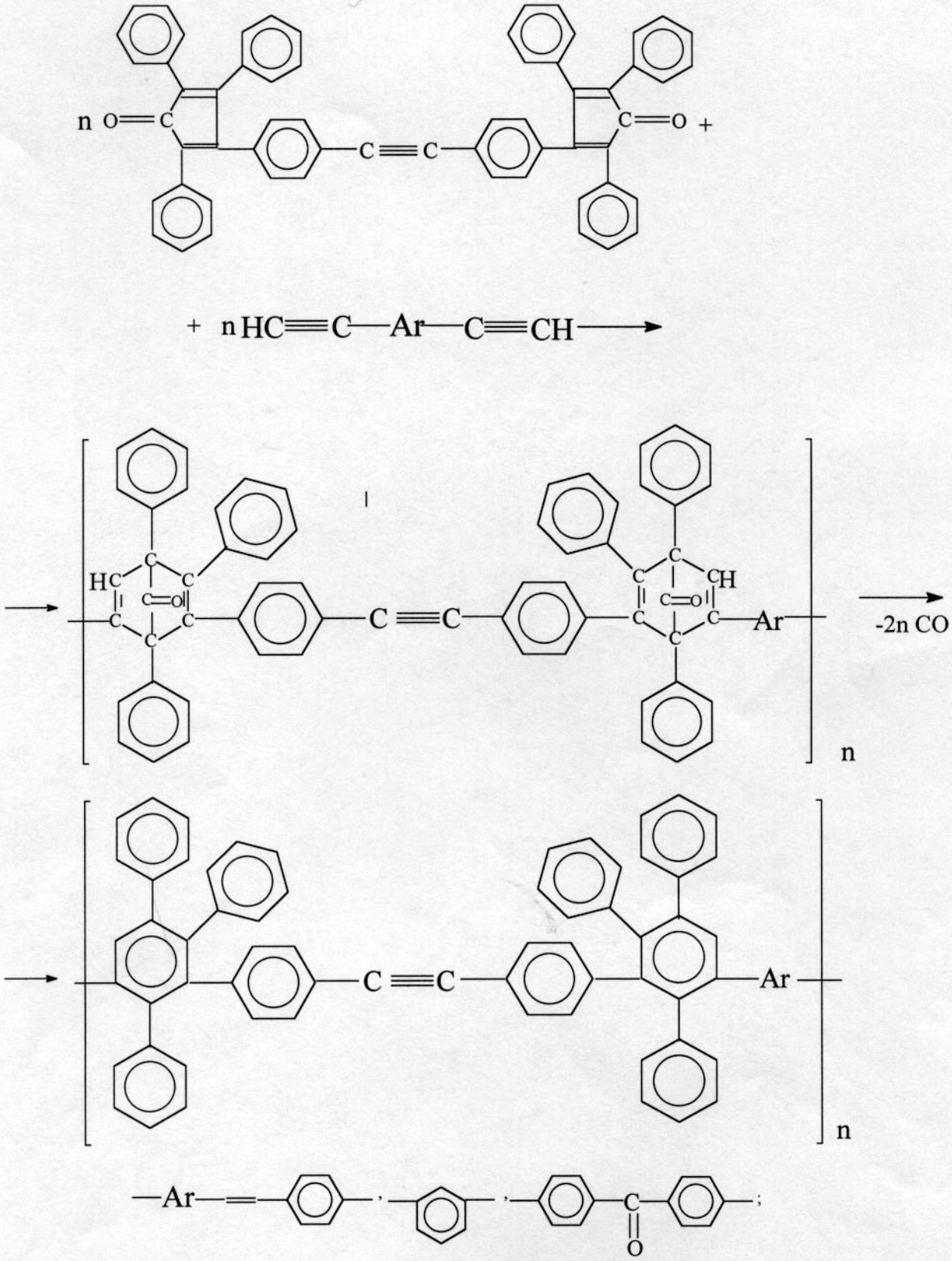

H2N
CF3
C
CF3
NH2
I
I
2
[O]
O
O
O
O
KOH


n
CF3
CF3
O
+ n HC≡C—Ar—C≡CH
-2n CO
n
Ar
n
-Ar-
C≡C

Some properties of phenylated polyphenylenes of general formula

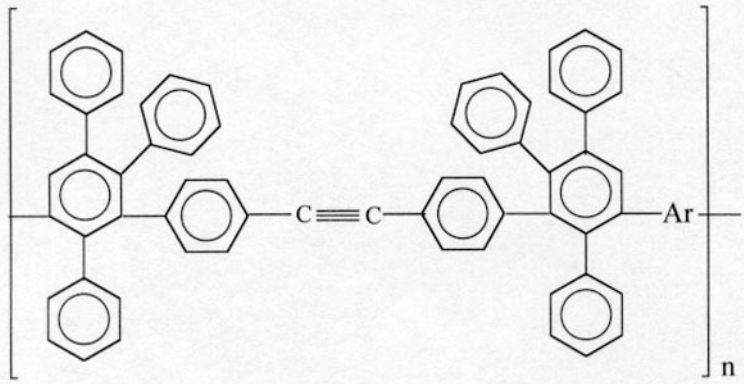


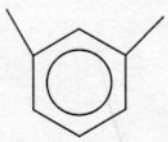
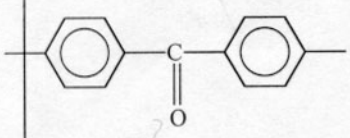
-Ar-	$\eta_{red.}$ (m-cresol, 25°C) dl/g	T_g °C	Mechanical Properties of Films		Dielectric constants		
			σ, %	ε, %	Calc.	RH= 0%	RH= 50%
	0.47	247	-	-	2.63	-	-
	0.80	260	50.0	3.2	2.63	2.55	2.56
	0.89	254	78.0	6.6	2.67	2.65	2.56



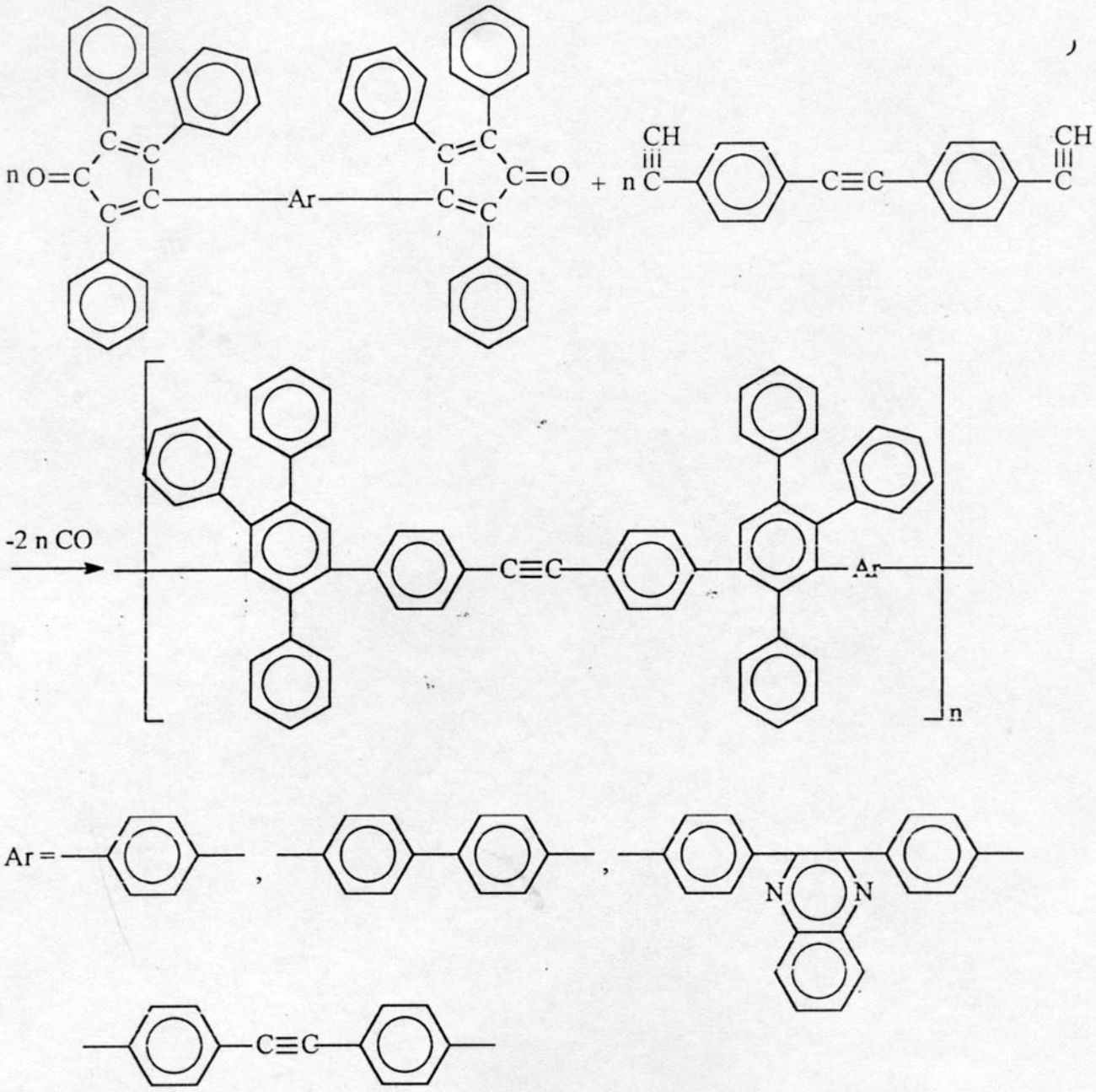
Reactions were carried out in 1,2,4-trichlorobenzene at 220° C for 40 hrs.

Table . Some properties of phenylated polyphenylenes of general formula



-Ar-	$\eta_{red.}$, dl/g	T g., °C	T 10%., (TGA, ΔT=4.5 °C/min,), °C		Films properties , 25°C	
			air	Ar	σ, MPa	ε, %
	0.62	345	590	645	6.50	5.0
	0.41	328	570	615	--	--
	0.51	330	591	630	6.80	6.5

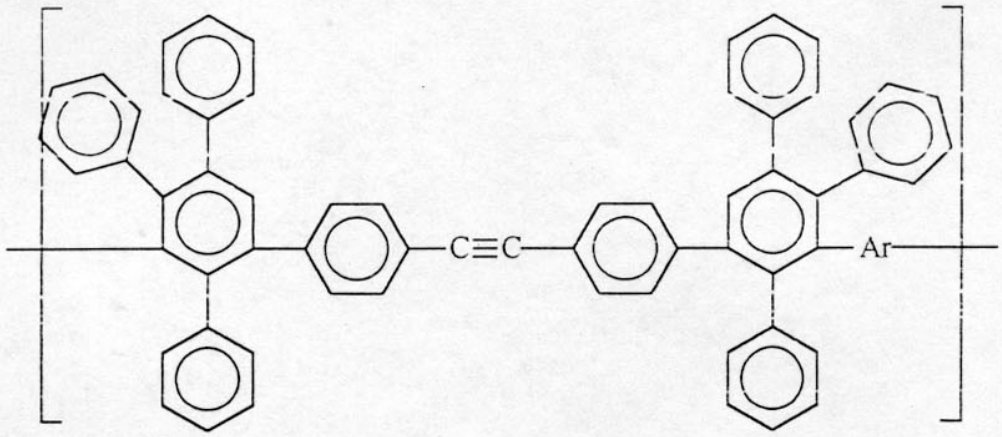
All polymers are soluble in N-MP, DMSO, DMA, DMF.

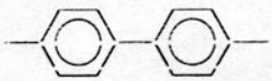
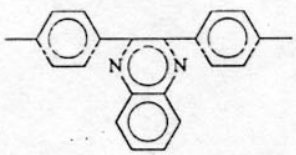
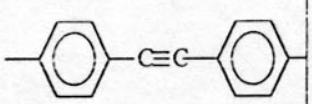


All polymers are soluble in N-MP, DMF and (except of the polymer based on 4,4'-diethynyltolane) in DMSO, m-cresol, THF, $CHCl_3$, toluene.

Table

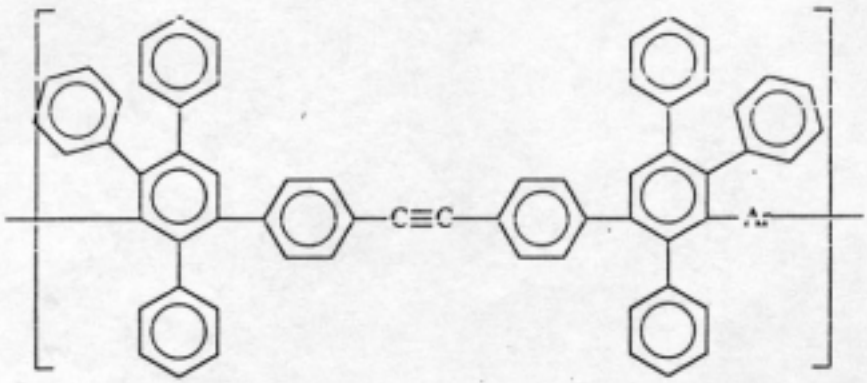
Properties of the polyphenyleneethynylenes of general formula



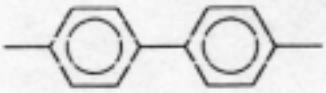
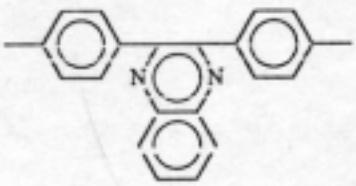
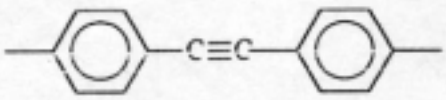
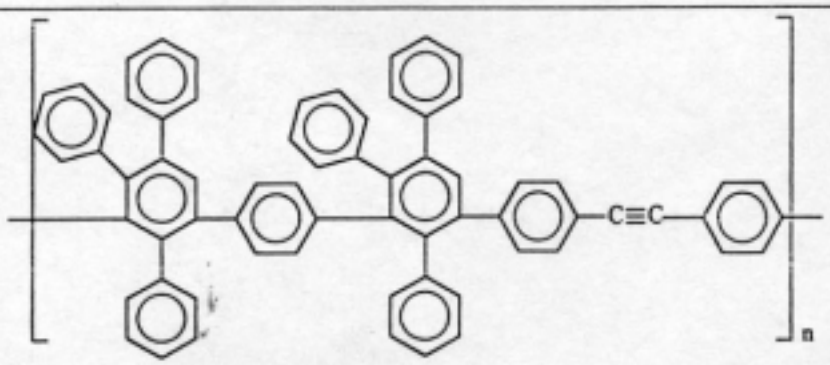
-Ar-	η_{red} (N-MP, 25°C) dl/g	Films properties (25°C)		Dielectric const (ε') at relative humidity		Tg °C	$T_{10\%}$, °C TGA, ΔT=10°/ min air/Ar
		σ, MPa	ε, %	0%	50%		
	0.91	69.8	8.1	2.85	2.90	340	564/614
	0.86	70.9	8.1	2.81	2.85	335	575/635
	0.41	BRITTLE FILM				318	569/621
	0.68	72.0	9.3	2.87	2.91	329	580/645

Table

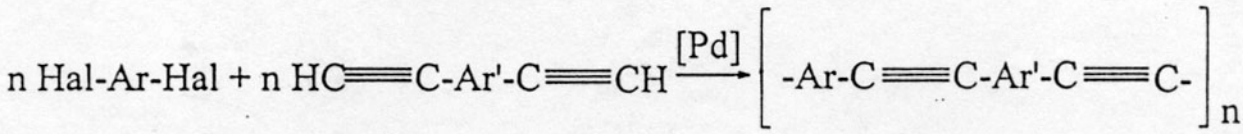
Absorption (λ_a) and fluorescence (λ_f) spectra for polyphenyleneethynylenes



films

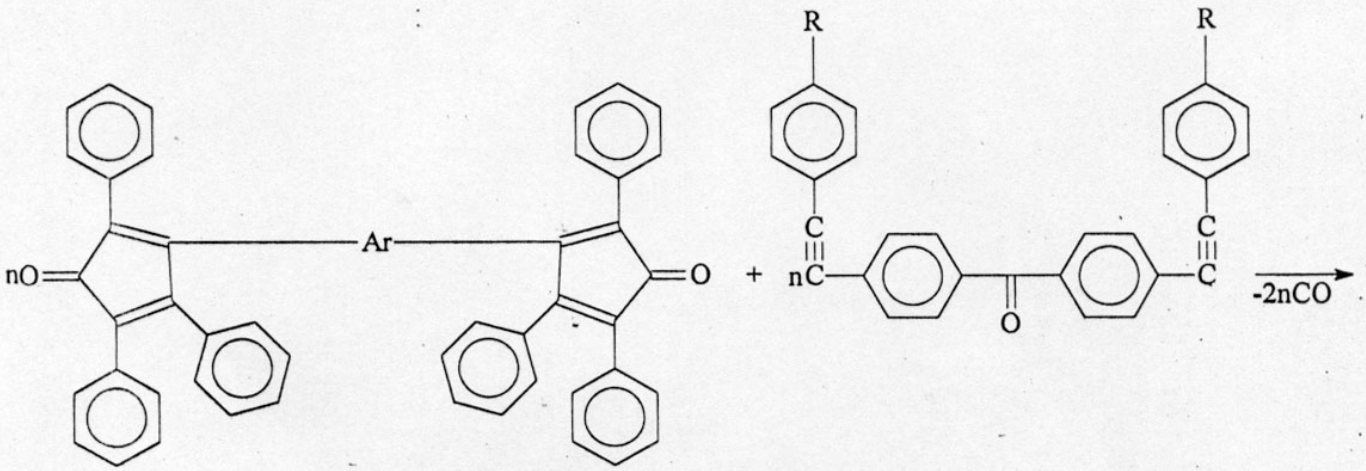
-Ar-	λ_a, nm	λ_f, nm
	435	548
	420	531
	426	540
	440	580
	438	562

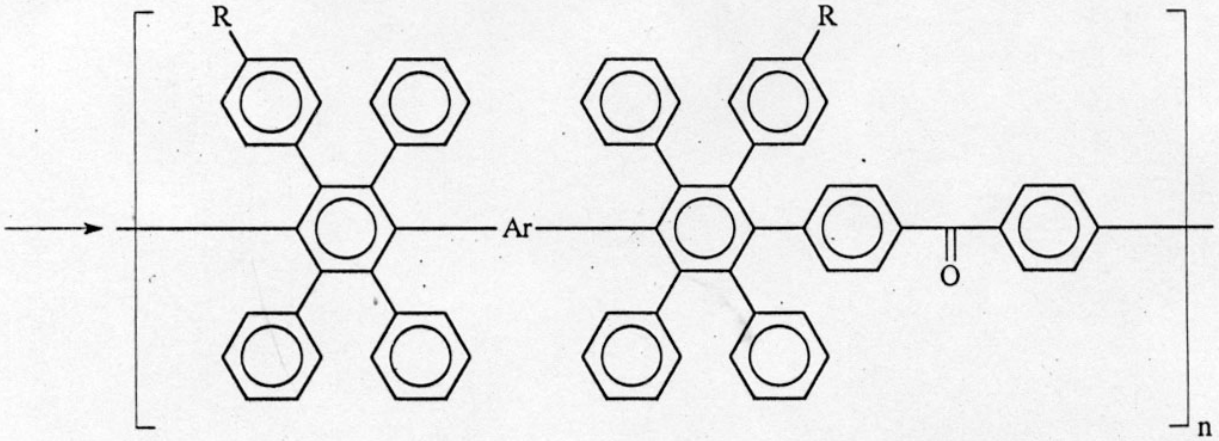
Polyphenyleneethynylenes and polyheteroaryleneethynylenes - polymers with promising electrooptical properties - usually are prepared by the interaction of dihaloaromatic and diethynylaromatic compounds catalyzed with transition metals (first of all - Pd) derivatives.

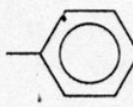
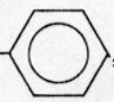
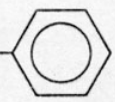
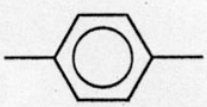


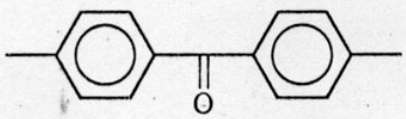
Because of the side reactions these procedures often lead to the formation of relatively low molecular weight polymers; in addition, preparation of organo-soluble polyphenyleneethynylenes and polyheteroaryleneethynylenes seems to be rather problematic.

In the frames of present investigation we have developed a new synthetic approach to the preparation of polyphenyleneethynylenes and polyheteroaryleneethynylenes. This approach is based on the utilization of acetylene-containing monomers - e.g. bis-α-diketones and bis-cyclopentadienones - in smoothly proceeding polymers - forming reactions - formation of polyphenylquinoxalines and phenylated polyphenylenes.

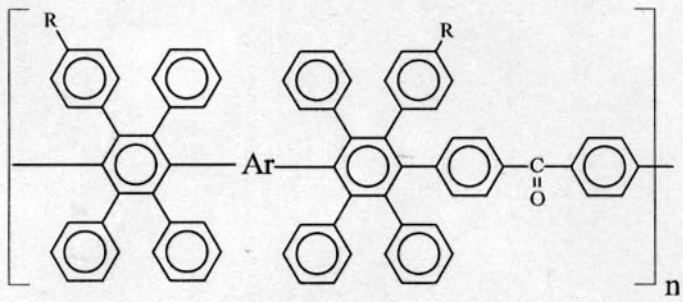


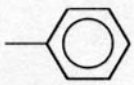
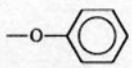
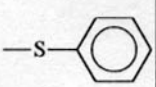
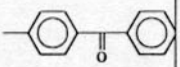
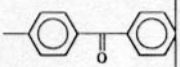
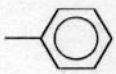
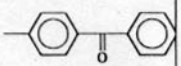
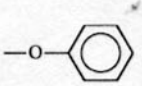
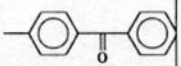
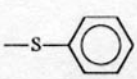


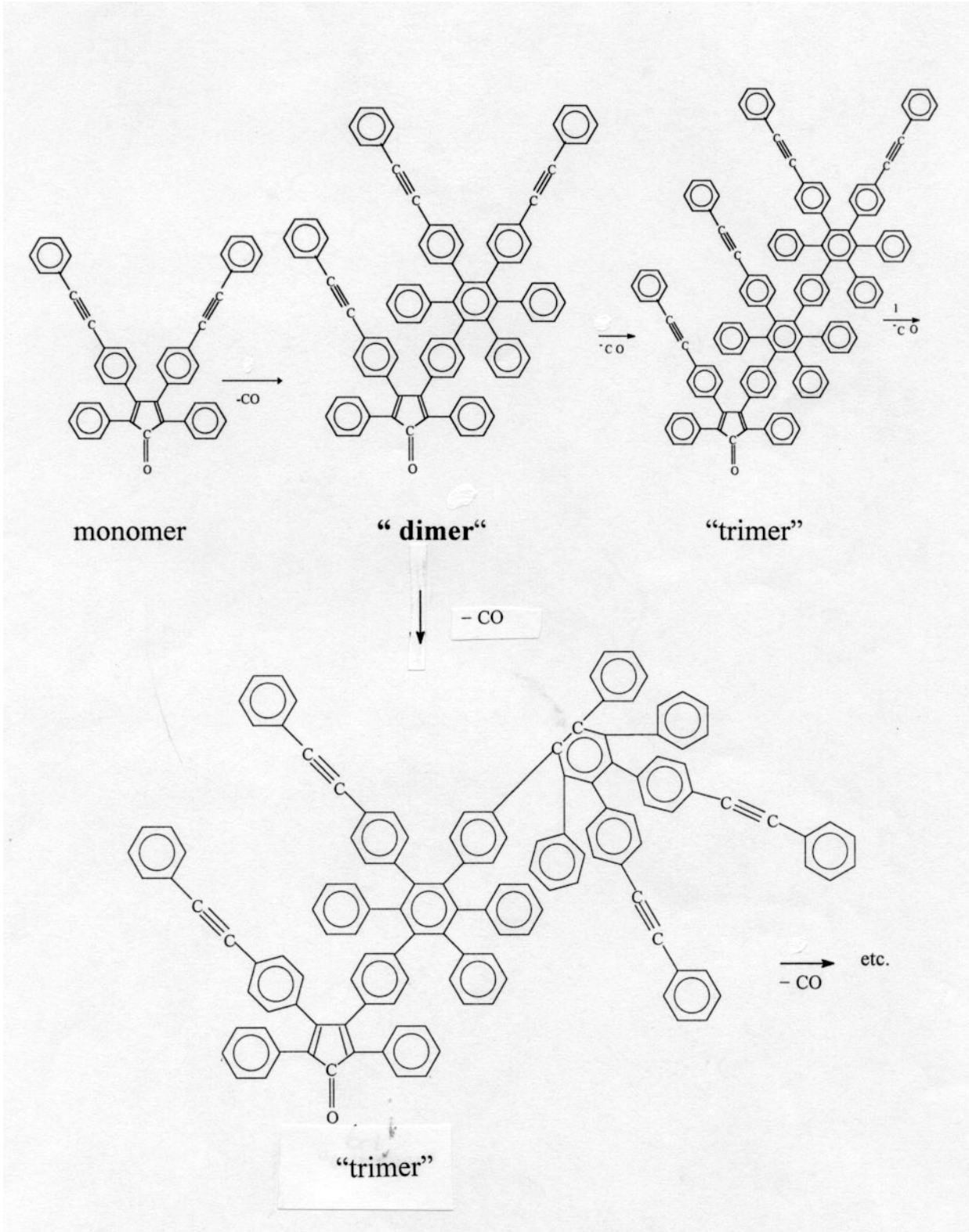
где R= —H,  , —O—  , —S—  ; Ar =  ,

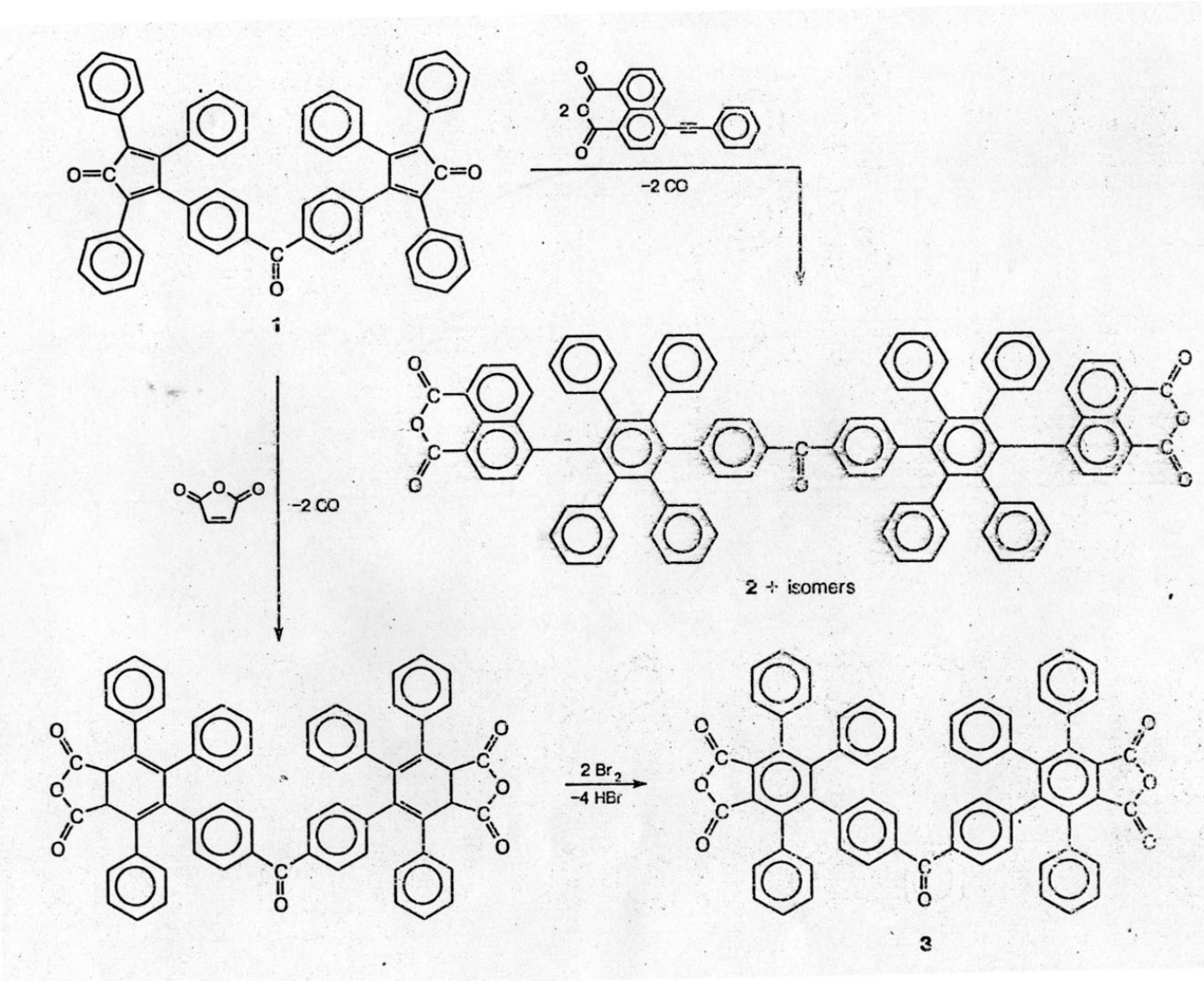


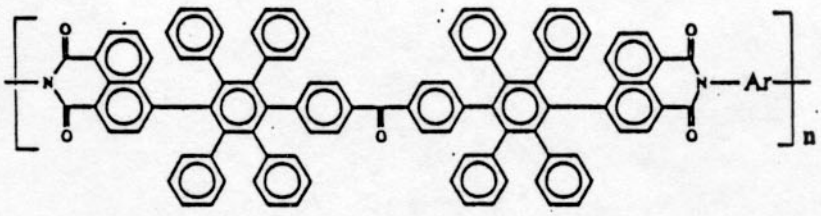
Некоторые характеристики фенилированных полифениленов IX общей формулы



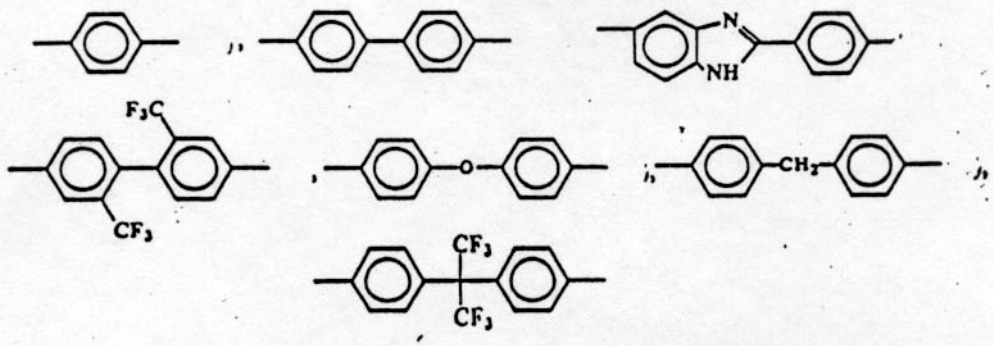
По ли мер	-Ar-	-R	M_w x10^{-3}	M_n x10^{-3}	$\frac{M_w}{M_n}$	$\eta_{прив}$, (ДМФА, 25°С,5 %), дл/г	T_c, °С	$T_{10\%}$-ной потери массы, °С	
								воздух	аргон
IXA		-H	63.70	24.30	2.62	0.44	365	565	642
IXБ			114.10	16.30	7.00	0.50	328	592	639
IXB			34.70	9.20	3.76	0.51	276	613	629
IXГ			40.30	13.10	3.08	0.43	229	530	581
IXД		-H	70.70	22.60	3.12	0.51	315	558	628
IXE			201.30	32.80	6.13	0.53	313	601	633
IXЖ			110.80	23.80	4.65	0.48	235	590	615
IXЗ			46.70	7.60	6.15	0.41	233	536	588

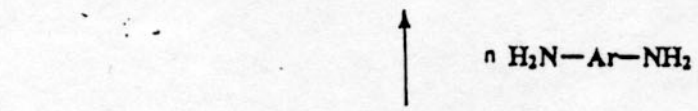

-CO
monomer
" dimer"
"trimer"
- CO
etc.
- CO
"trimer"


2
-2 CO
1
-2 CO
2 + isomers
2 Br2
-4 HBr
3

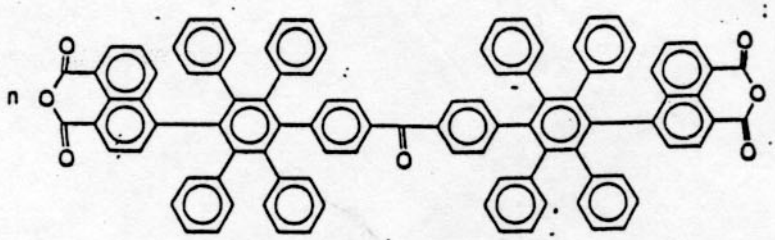


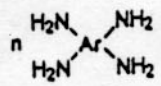
Ar =

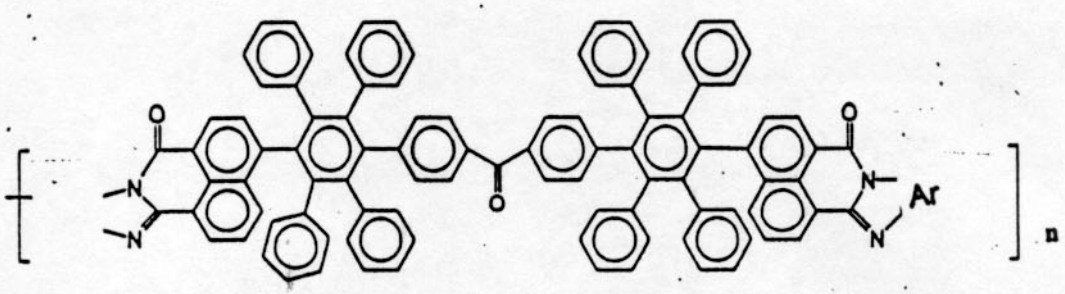




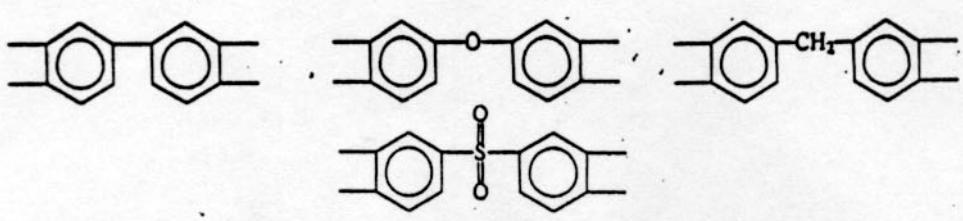
n $H_2N-Ar-NH_2$







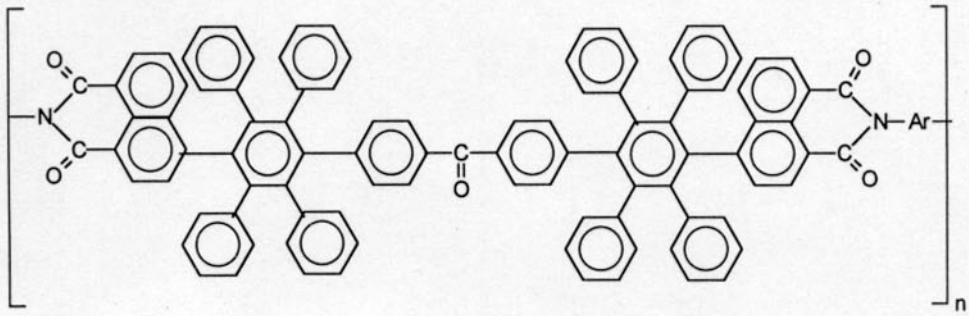
—Ar—

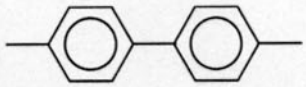
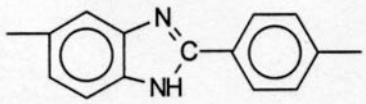
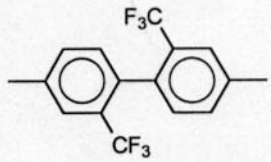
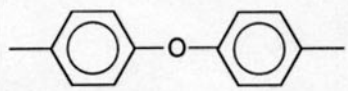
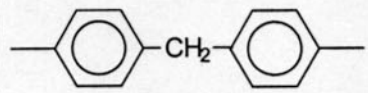
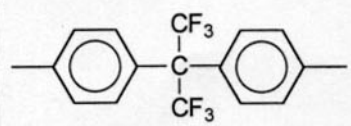


All polyimides syntheses were carried out in m-cresol using benzoic acid as catalyst at 180 °C for 10 hrs. Syntheses of polynaphthylimides and polynaphthoylenebenzimidazoles were carried out in m-cresol using benzoic acid + benzimidazole as catalyst at 180°C for 10 hrs.

All polycondensation reactions proceeded homogeneosly and led to the formation of high molecular weight polymers in almost quantitative yields.

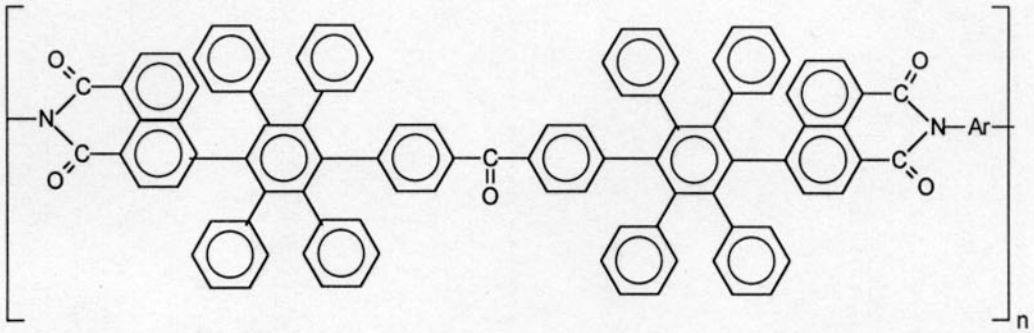
Table. Solubilities and viscosities of the polyimides of general formula:



-Ar-	$\eta_{red.}$, DMF, 25°C, dl/g	Solubility						
		NMP	m-cresol	DMSO	THF	DMAA	$CHCl_3$	C_6H_5-CH_3
	0.76	+	+	+	+	+	+	++
	0.71	+	+	+	+	+	+	++
	0.62	+	-	+	+	+	-	-
	0.52	+	+	+	+	+	+	++
	0.78	+	+	+	+	+	+	++
	0.71	+	+	+	+	+	+	++
	0.73	+	+	+	+	+	+	++

+ Soluble; ++ soluble on heating; - insoluble

Table. Mechanical and electrical properties of the films based on polyimides of general formula:



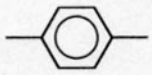
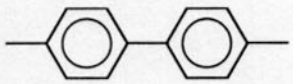
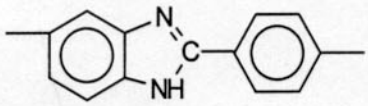
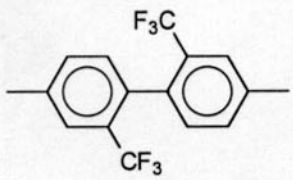
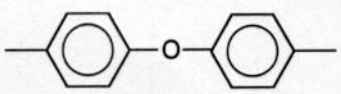
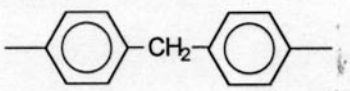
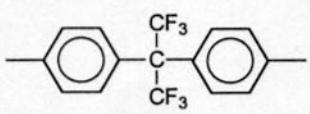
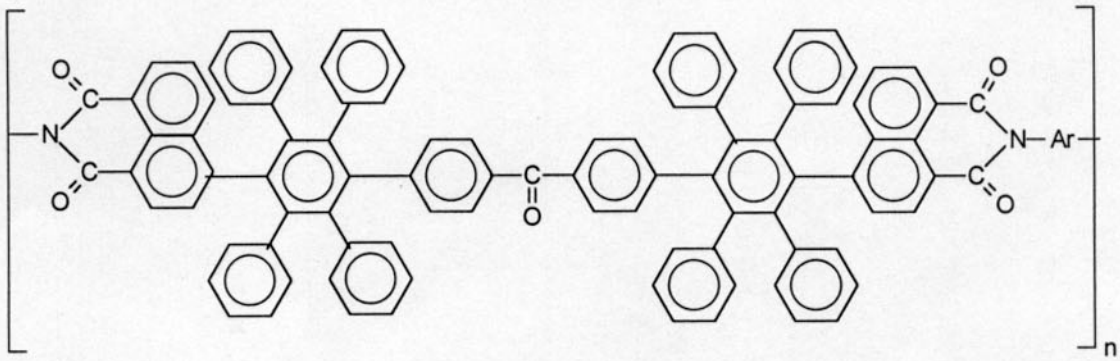
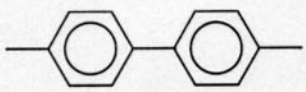
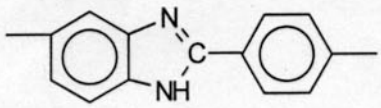
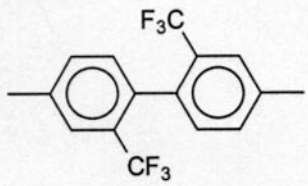
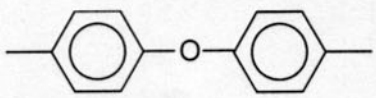
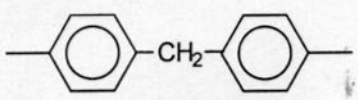
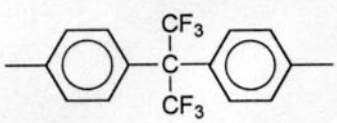
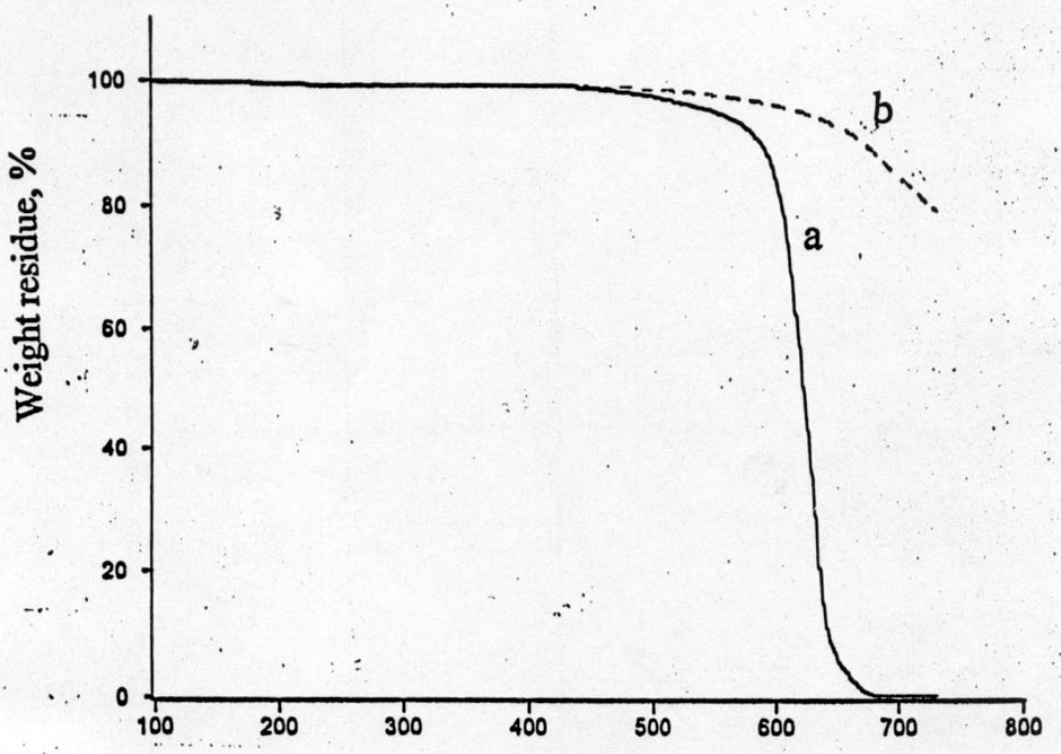
-Ar-	Mechanical properies at 25°C			Dielectric Constants, ε′		
	σ, MPa	ε, %	E, GPa	Calc.	RH 0 %	RH 50%
	79.5	6.0	2.55	2.87	2.95	3.17
	83.0	3.0	1.80	2.86	2.89	3.19
	66.1	6.0	2.17	2.97	3.00	3.25
	82.0	9.0	1.55	2.81	2.85	2.91
	69.0	4.0	1.76	2.88	3.00	3.28
	70.0	8.0	1.60	2.86	2.91	3.30
	65.0	4.5	1.70	2.82	2.80	2.95

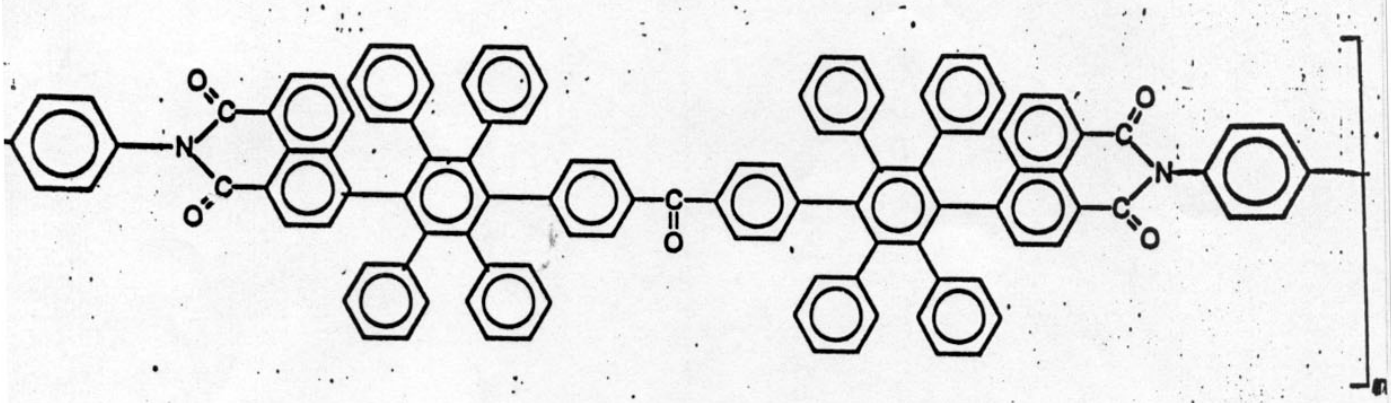
Table. Thermal properties of the polyimides of general formula:



-Ar-	T_g, °C	$T_{10\%}$, °C (TGA)		$T_{10\%}$-T_g	$T_{10\%}$-T_g
		Air	Ar	Air	Ar
	375	613	680	238	305
	398	588	663	190	265
	389	614	629	225	240
	385	605	662	220	277
	370	589	669	219	299
	340	583	647	243	307
	380	595	626	215	246



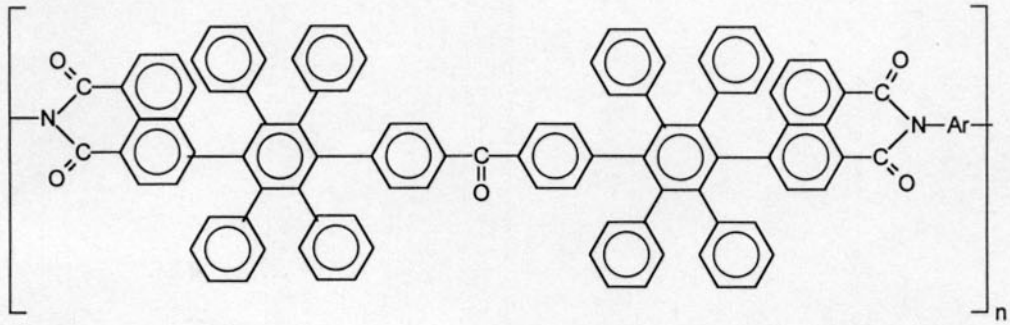
TGA curves for polynaphthoylimide

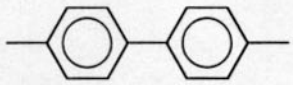
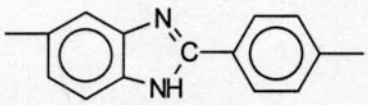
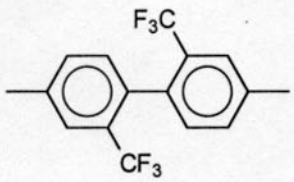
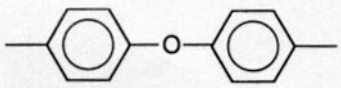
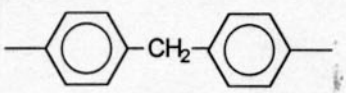
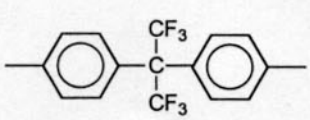


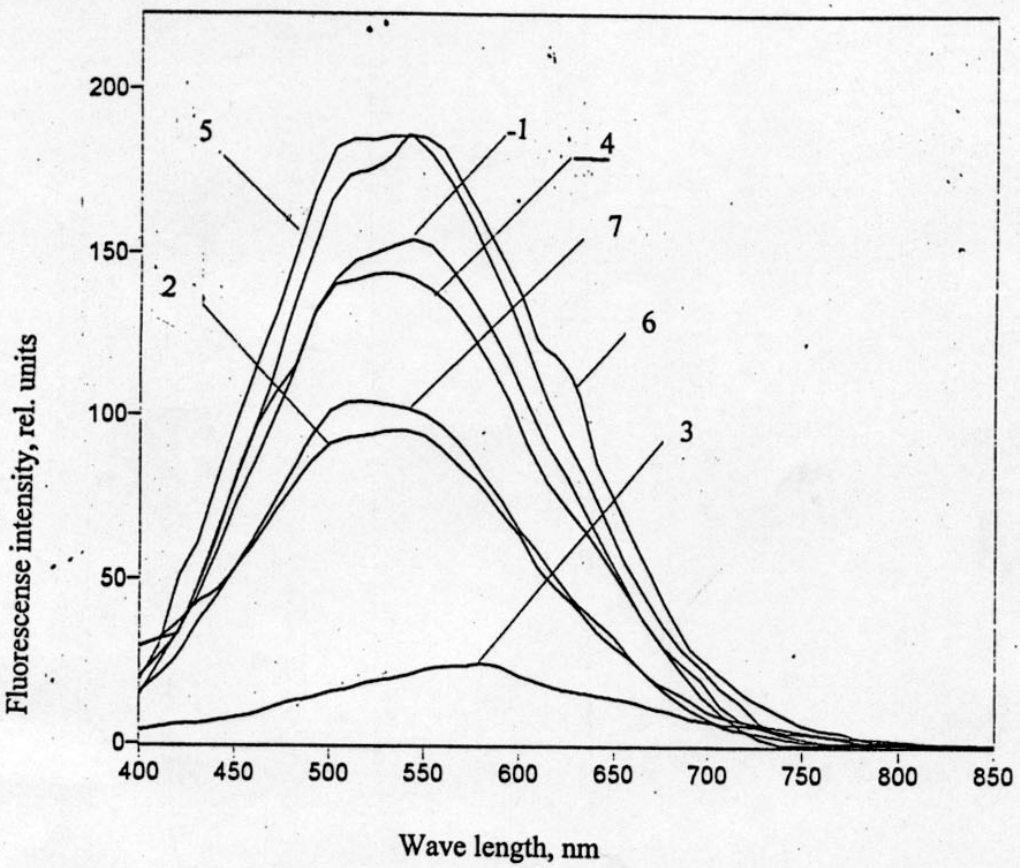
in air (a) and in argon (b)

ΔT= 20°/min.

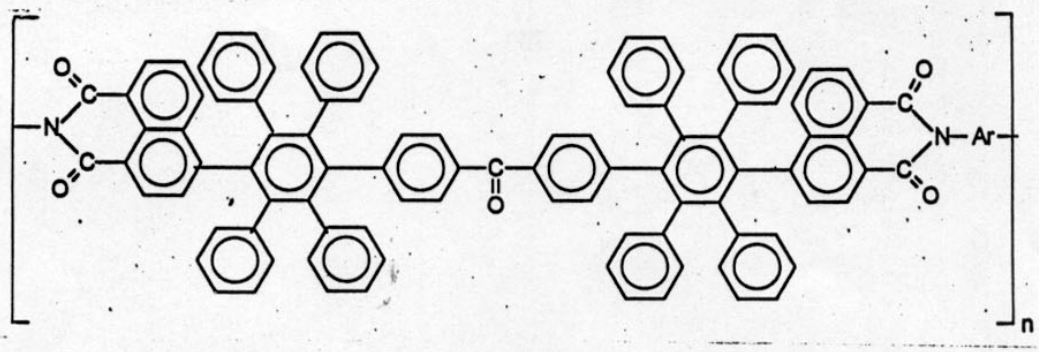
Table. Photoabsorption and fluorescent characteristics of the polynaphthylimides of general formula:

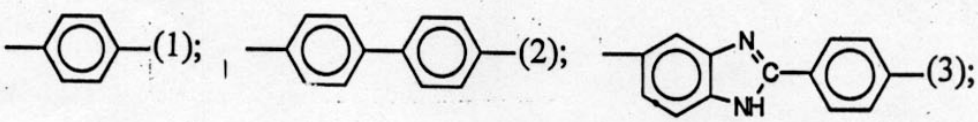


-Ar-	λ_a, max, nm	λ_f, max, nm	Relative quantum yield
	408	550	6.1
	400	540	3.8
	431	580	1.0
	410	530	5.6
	415	510,548	7.3
	421	510,550	7.3
	399	510	4.1



Fluorescence spectra for polynaphthylimides of general formula



-Ar- =  (1); (2); (3);

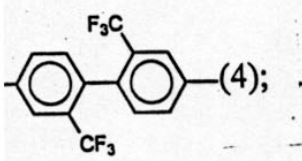
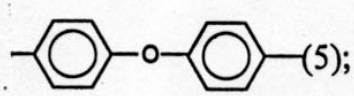
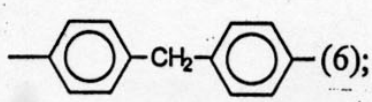
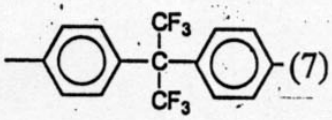
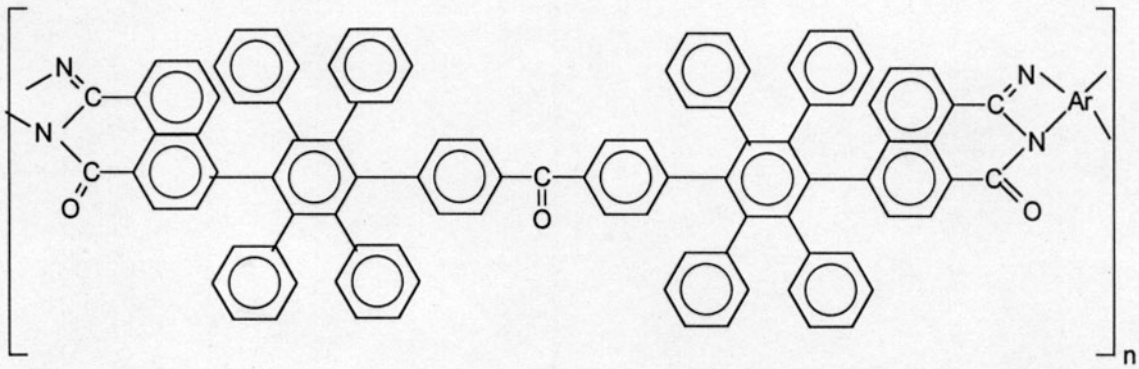
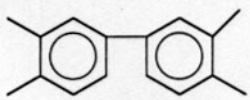
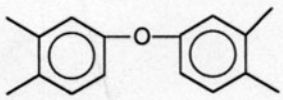
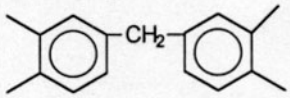
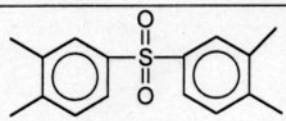
 (4);  (5);  (6);  (7)

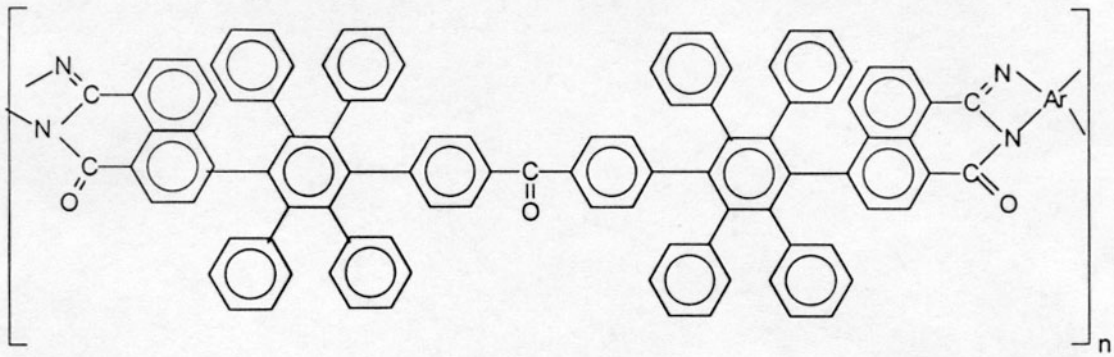
Table. Solubility and viscosities of polynaphthoylenebenzimidazoles of general formula:



Ar	$\eta_{red.}$ (NMP, 25°C), dl/g	Solubility					
		DMF	DMSO	m-cresol	THF	C_5H_5N	$CHCl_3$
	0.80	+	+	+	+	±	+
	0.72	+	+	+	+	±	+
	0.91	+	+	+	+	±	+
	0.69	+	+	±	±	±	-

+ soluble; ± partially soluble; - insoluble

Table. Mechanical and electrical properties of the films prepared from polynaphthoylenebenzimidazoles of general formula:



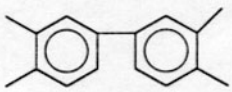
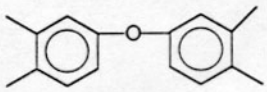
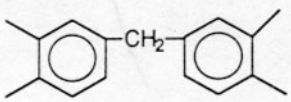
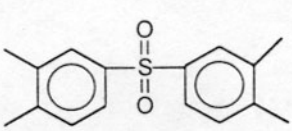
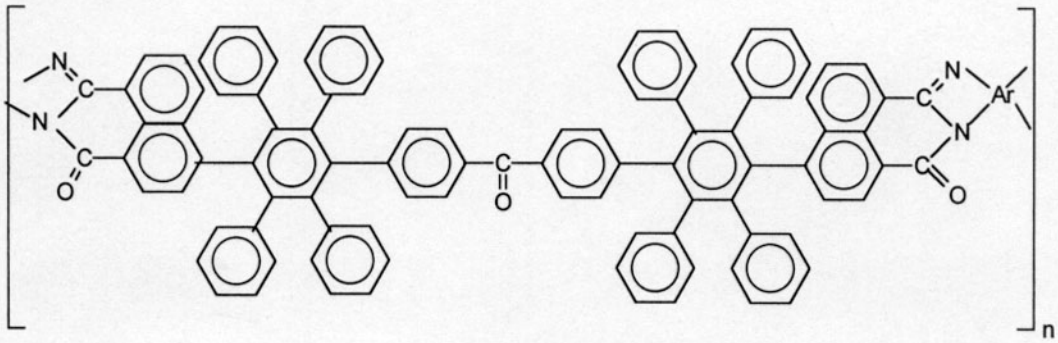
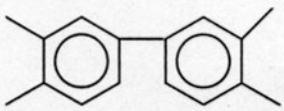
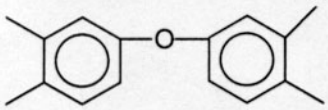
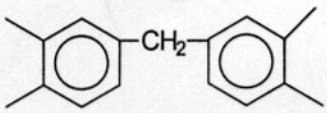
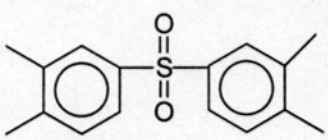
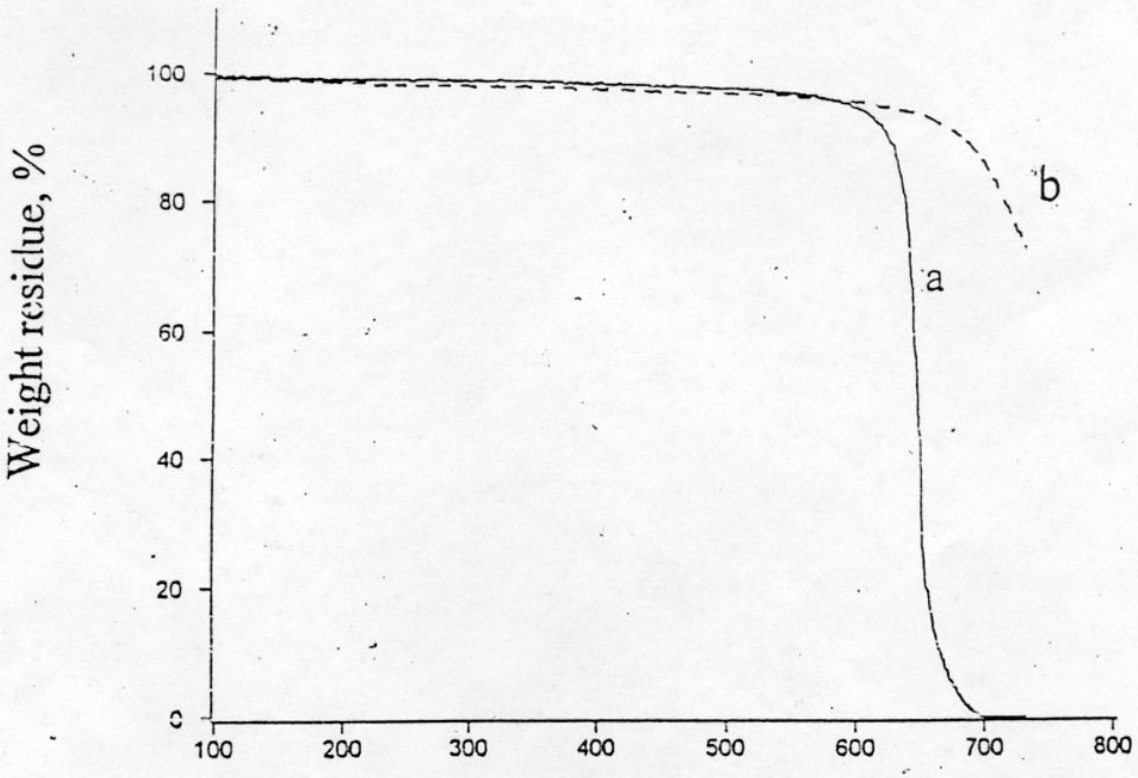
Ar	Mechanical properties			Dielectric constants, ε′	
	σ, Mpa	E, GPa	ε, %	RH=0%	RH=50%
	68.8	2.25	5.5	3.10	3.53
	61.7	2.10	5.0	3.13	3.54
	62.4	2.21	4.8	3.16	3.58
	61.0	2.00	4.5	3.20	3.61

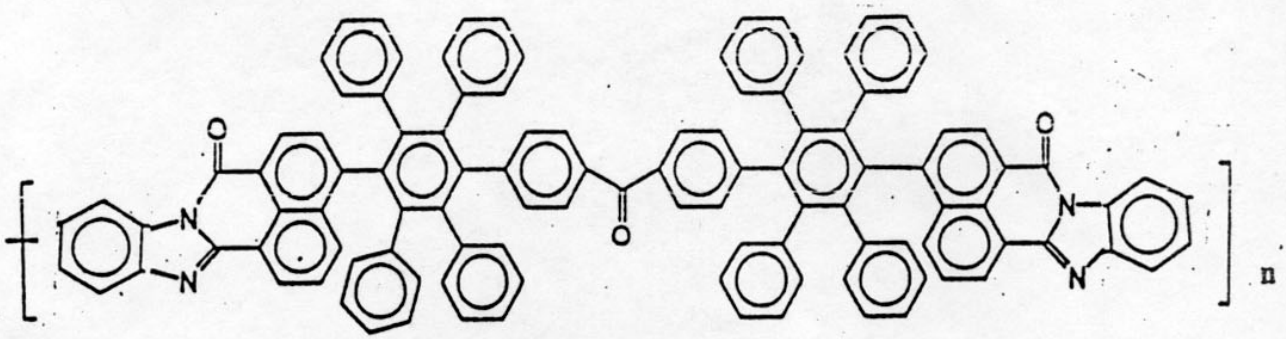
Table. Maximums of absorption and fluorescence spectra for polynaphthoylenebenzimidazoles of general formula:



Ar	λ^a max, nm	λ^f max, nm
	510	595
	500	580
	500	590
	510	578



TGA curves for polynaphthoylenebenzimidazole



in air (a) and in argon (b)

$\Delta T=20°C$