Russian Chemical Reviews **68** (8) 685 – 696 (1999) © 1999 Russian Academy of Sciences and Turpion Ltd

UDC 561.64

New condensation polymers having low dielectric constants

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Abstract. The review considers factors that determine the dielectric properties of the medium as well as the basic approaches to the preparation of film materials with low dielectric constants based on condensation polymers that contain fluorinated and/or alicyclic units and of polymeric nanofoams. The bibliography includes 147 references.

I. Introduction

Nowadays, the problem of creating film materials with reduced dielectric constants which can be used as interlayer dielectrics (ILD) in packages of multiintegrated circuits is becoming ever more topical.[1,2] It is known that the velocity of electrical pulses is inversely proportional to $\varepsilon^{1/2}$, where ε is the dielectric constant (DC) of the medium.[3,4] In addition, the minimum distance between the lines in integrated circuits is limited by 'noises' arising because of the 'cross effect' dependent on the DC of the insulating material, *i.e.*, currents elicited in conductors near the active signal lines. For this reason, a decrease in ε results in the reduction of the machine cycle, and it becomes possible to increase the density of integrated circuits. One of the materials most widely used for ILD is silicon dioxide for which ε ranges from 4 to 10 depending on moisture content. Materials with ε values lower than that of SiO_2 are divided into four basic groups:[4]

SiO_2 modified by fluorine treatment ($\varepsilon = 3.0 - 4.0$);
organic polymers ($\varepsilon = 2.0 - 3.0$);
nanofoams of organic polymers ($\varepsilon = 1.1 - 3.0$);
SiO_2 aerogels ($\varepsilon = 1.1 - 4.0$).

Additionally, the materials for ILD should meet the requirements for manufacture technologies and operation of circuit elements. These include high thermal stability and mechanical strength in combination with low thermal expansion and residual stress in the thermal cycle. Organic condensation polymers meet these requirements the best, and this review is devoted to the analysis of major achievements in these directions.

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Received 23 November 1998
Uspekhi Khimii **68** (8) 760 – 772 (1999); translated by V D Gorokhov

II. Factors influencing the dielectric constants of polymers

The dielectric constant of polymers is mainly influenced by their free volume,[5] polarisability[6] and hydrophobicity.[7]

An increase in the free volume may be regarded as replacement of a portion of a polymer ($\varepsilon \simeq 3$) by air ($\varepsilon = 1$) resulting in a decrease in DC of the material.

The ε value of any material is proportional to the total polarisability (α_{tot}), and ε increases with the increase in α_{tot}. The total polarisability includes components of three types of polarisation: electronic (α_e), atomic (α_a) and resulting from dipole orientation (α_0):[5–8]

$$\alpha = \alpha_e + \alpha_a + \alpha_0.$$

The total dielectric constant ε is also the sum of increments related to each type of polarisation

$$\varepsilon = \varepsilon_e + \varepsilon_a + \varepsilon_0.$$

Electronic polarisation is determined by a slight deviation from the equilibrium distribution of electrons relative to the positively charged nuclei with which they are associated.[5–8] As this process includes only the motion of electrons, it can occur very fast, and usually the time constant is $\sim 10^{-13}$ s. At optical frequencies, where only optical polarisation can take place, the Maxwell equation operates:

$$\varepsilon = n^2,$$

where n is the refractive index.

Atomic polarisation results from changes in the disposition of atomic nuclei under the action of an electric field. This type of polarisation is characterised by a typical time constant of $\sim 10^{-13}$ s. For solid organic compounds, the contribution of α_0 to the total polarisation accounts for $\sim 10\%$ of α_e.[5–8]

The polarisation resulting from dipole orientation is the consequence of redistribution of charges, *i.e.*, reorientation of a group of atoms with a constant dipole moment in space under the action of an electric field. Since reorientation involves large-mass particles, the process proceeds more slowly than the electronic or atomic polarisation and is characterised by a time constant of $\sim 10^{-9}$ s even in the gas phase. In this case, it is necessary to overcome high inertia for changing the direction of motion in each cycle of the electrical field oscillation. In the liquid phase and to a larger extent in the solid phase, intermolecular friction forces operate, which also decelerate the process and decrease the α_0 values characteristic of the static conditions.

The polarisation resulting from dipole reorientation often makes the major contribution to the formation of ε values of fluids and gases; however, in solids the contribution from α_e is often more substantial. Naturally, in solids the mobility of dipoles, which depends on the frequency and temperature of measurements, is increased at temperatures above the glass transition temperature T_g, though appreciable motion of dipoles may also occur below T_g due to β-transitions.[8]

The dielectric properties of polymers are also dependent on their hydrophobicity,[7,9,10] since orientation of water dipoles occurs readily and is retained up to high frequencies of the electrical field (10^{13} Hz for free water). In addition, a water-containing polymer may be regarded as a composite material in which one component (water) has DC equal to 80,[7] which makes an appreciable contribution to the additive value of ε_{tot} of this material.

Thus, hydrophobicity of polymers can play an important role in the formation of electrophysical properties of materials.

The contributions from the above-listed factors to DC values of polymers can differ substantially on going from one structure to another. Thus the contribution of free volume to the DC of polyimides can vary from 25% to 94% depending on the polymer structure.[5]

III. Condensation polymers with low dielectric constants

Aromatic hetero- and especially carbon-chain polymers (CP) are the most promising materials for the creation of ILD. The greatest attention of researchers was attracted to hydrophobic and non-polarisable fluorinated CP and to polymers with cycloaliphatic fragments. The dependence of ε on the frequency of measurements, temperature and moisture creates certain difficulties in the establishment of a clear-cut dependence of DC on the structure of polymers. Nonetheless, the available experimental data make it possible to reveal basic regularities and dependences in the structure – DC relationships for a broad range of CP. As most of the studies analysed in this review are concerned with the film-forming (*i.e.*, high-molecular-weight) systems, the influence of the degree of polymerisation on the properties of the materials was not considered.

1. Fluorine-containing condensation polymers

Introduction of fluorine into macromolecules of carbochain polymers results in an increase in their hydrophobicity and free volume with a concomitant decrease in their polarisability.[7] Of different approaches to the introduction of fluorine into macromolecules, those based on the use of monomers with the hexafluoropropane-2,2-diyl groups (HFPG) are the most popular.[11–16]

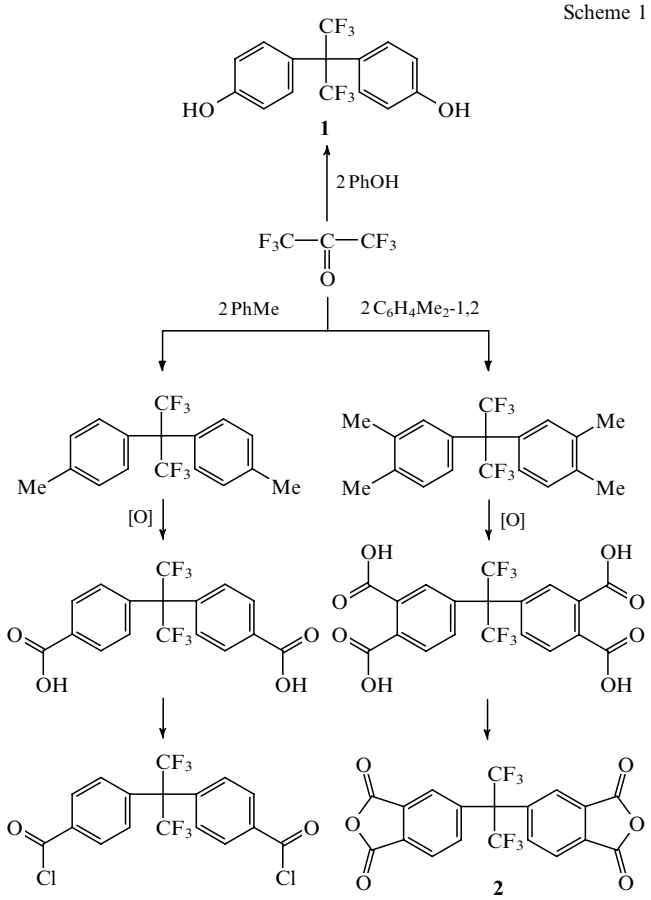
The first representatives of HFPG-containing monomers, *viz.*, 1,1,1,3,3,3-hexafluoro-2,2-bis(4-hydroxyphenyl)propane (**1**), 1,1,1,3,3,3-hexafluoro-2,2-bis(4-carboxyphenyl)propane and its dichloro and 1,1,1,3,3,3-hexafluoro-2,2-bis(3,4-dicarboxyphenyl)propane dianhydride (**2**), were synthesised starting from hexafluoroacetone according to Scheme 1.

These monomers are either used directly for the preparation of aromatic CP or are applied for the synthesis of more complex HFPG-containing monomers.[14] In addition to HFPG, trifluoromethyl[17–20] and other perfluoroalkyl[17,21] substituents and perfluoroaromatic fragments[17,22–24] were incorporated into macromolecules.

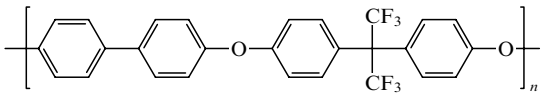
Among fluorinated aromatic condensation polymers with reduced DC, aromatic polyethers (APE) and polyimides are the most interesting.

The most popular method for the synthesis of APE is nucleophilic aromatic polysubstitution[25–27] with bisphenoxides and activated dihalogenoaromatic or dinitroaromatic compounds as the starting reagents.

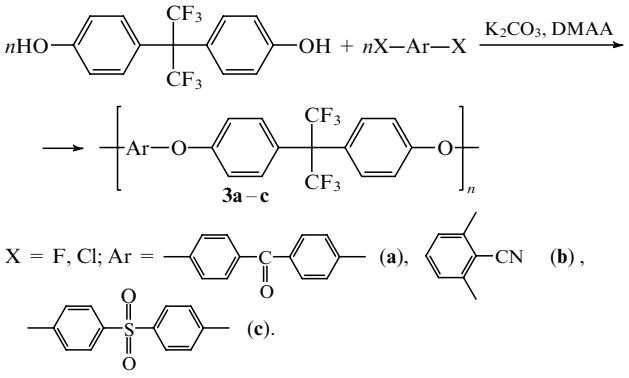
Scheme 1



The first fluorine-containing APE



was the polycondensation product of disodium bisphenoxide **1** with 4,4′-dibromobiphenyl.[28] Fluorine-containing APE of the general formula **3** were obtained by the reaction of dipotassium bisphenoxide **1** with 4,4′-difluorobenzophenone, 2,6-difluorobenzonitrile and bis(4-chlorophenyl) sulfone.[22,29,30]



The dielectric constant of APE **3a – c** characterised by a moisture absorption of ~ 0.9% varies from 2.94 to 3.03 at a relative humidity (r) equal to zero (Table 1). Comparatively high values of ε for APE **3a – c** are determined by the presence of such polarisable groups as carbonyl, sulfonyl and nitrile groups in their molecules.

The reaction of dipotassium bisphenoxide **1** with bis(4-fluorobenzophenone)-based monomers containing the amide,

Scheme 2

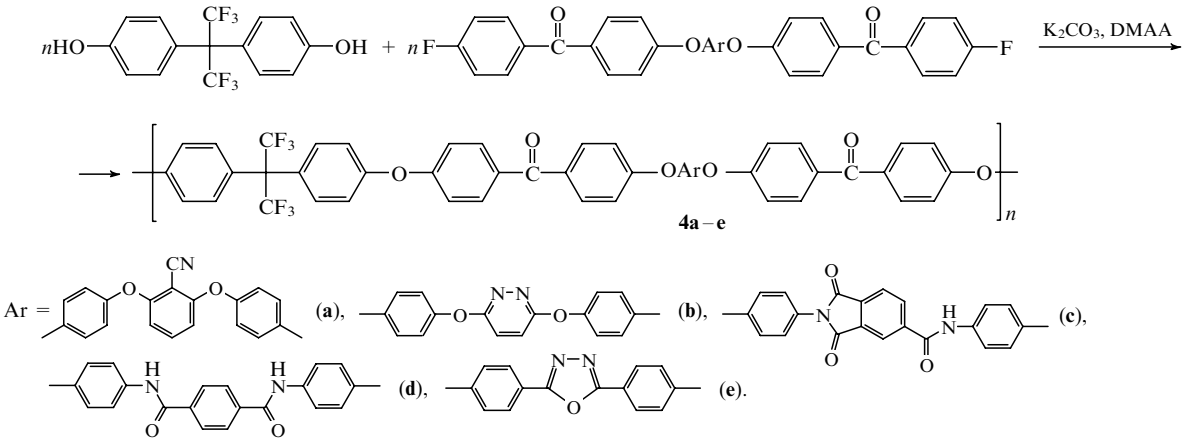


Table 1. Moisture absorptivity and DC of fluorine-containing APE.[22]

Polymer	Moisture absorption (%)	ε	
		$r = 0$	humid medium
3a	0.91	2.94	3.25 (r = 57.5%)
3b	0.78	2.99	3.39 (r = 67.3%)
3c	1.21	3.03	3.63 (r = 69.0%)

amido-imide, nitrile, 1,3,4-oxadiazole and pyridazine fragments (Scheme 2, see Ref. 31) yielded APE **4a**–**c** belonging to the class of polyetherketones (PEK), which are being intensively studied in the last decades.[32]

Films based on these polymers are elastic and thermostable. At $r = 0$, the dielectric constant of PEK **4a**–**e** varies from 3.02 to 3.54 (measurements at 10 kHz) (Table 2). The dependence of ε on r for PEK **4a** is presented in Fig. 1.

Table 2. Glass transition (T_g) and destruction temperatures (T_d) and DC of fluorine-containing polyetherketones **4**.[31]

Polymer	T_g /°C	T_d /°C	ε	
			$r = 0$	humid medium
4a	162	497	3.02	3.51 (r = 70%)
4b	176	498	3.09	3.53 (r = 70%)
4c	146	409	3.11	4.73 (r = 54%)
4d	185	458	3.51	4.54 (r = 54%)
4e	164	366	3.54	4.15 (r = 52%)

Polymers obtained using decafluorobenzophenone as the electrophilic monomer have considerably better characteristics. Thus PEK containing the perfluoroaromatic fragments and

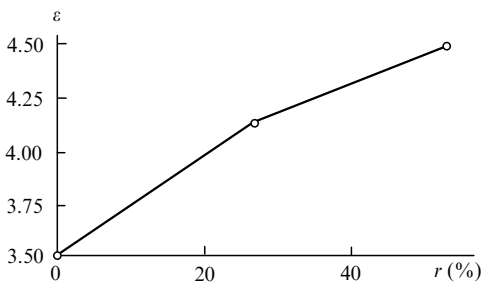
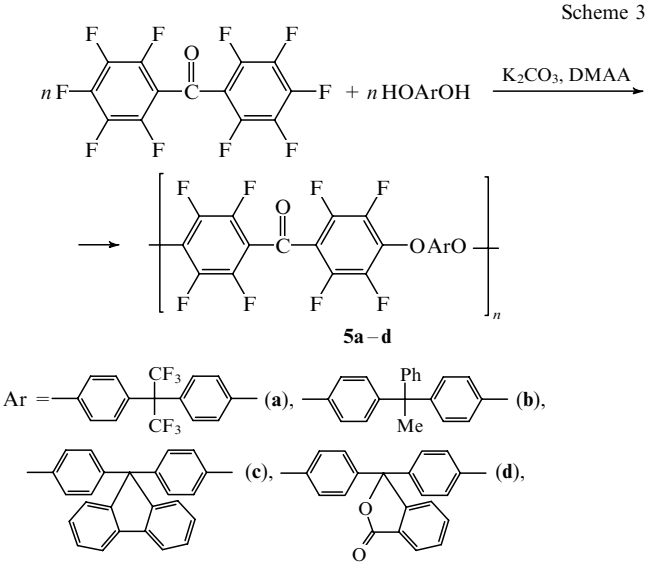


Figure 1. Dependence of dielectric constant on relative humidity for polyetherketone **4a**.

Scheme 3



obtained according to Scheme 3[33] possess rather high thermal stability, while the values of ε vary from 2.68 to 2.98 at $r = 0$ and from 2.79 to 3.10 at r = 68% (Table 3). The dependences of ε on r for PEK **5a**–**d** are presented in Fig. 2. Comparison of Figs 1 and 2 shows that an increase in r results in an increase in the values of ε for fluorinated APE and PEK, this being particularly pronounced for polymers with high moisture absorptivity.

Table 3. Glass transition and destruction temperatures and DC of fluorinated polyetherketones **5**.[33]

Polymer	T_g /°C	T_d(air) /°C	ε	
			$r = 0$	r = 68%
5a	155	425	2.68	2.79
5b	175	442	2.75	2.95
5c	223	436	2.80	3.00
5d	215	359	2.98	3.10

To make the dielectric constant of polymers still lower, it is necessary to remove the polar carbonyl groups from their macromolecules. For this purpose, perfluorinated aromatic hydrocarbons such as hexafluorobenzene[34–37] and especially decafluorobiphenyl (**6**)[22–24,38–45] were used instead of decafluorobenzophenone for the synthesis of APE.

Synthesis of APE based on **6** was carried out according to Scheme 4.[22,24]

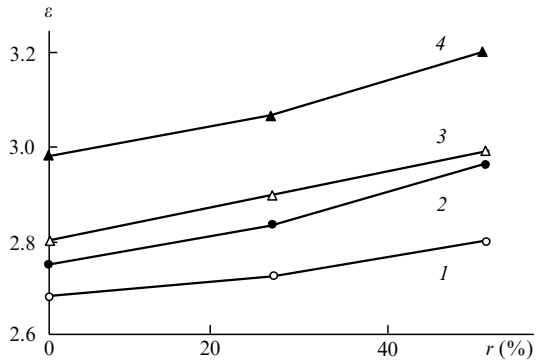
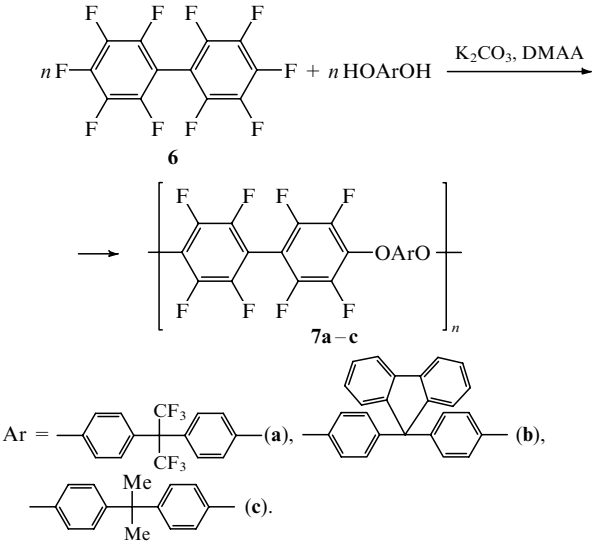


Figure 2. Dependence of dielectric constant of fluorine-containing polyetherketones **5a** (*1*) **5b** (*2*) **5c** (*3*) **5d** (*4*) on relative humidity.[33]

Scheme 4



6

7a–c

A slight excess of **6** was used to prepare polymers with the terminal nonafluorobiphenylyl groups. Some characteristics of fluorinated APE **7a**, **b** are presented in Table 4.

Table 4. Electrical and mechanical properties of APE based on decafluorobiphenyl.[40]

Property	Polymer	
	7a	**7b**
T_g /°C	189	260
Moisture absorptivity (%)	0.1	0.15
ε (ν = 10 kHz)		
r = 0	2.50	2.62
r = 60%	2.62	2.66
Thermal expansion coefficient α /ppm (°C)$^{-1}$	76	65
T_d (DTGA) /°C		
in air	500	500
in a nitrogen atmosphere	510	540
Loss of mass at 1000 °C in air (%)	60	37.5
Isothermal loss of mass in air (%)		
3 h at 400 °C	2.5	2.7
3 h at 450 °C	19.8	3.6
Tensile elongation Δl (%)	85.0	36.0

Aromatic polyethers of general formula 7 are linear or slightly branched (due to the reaction of more than two fluorine atoms with bisphenoxides) polymers soluble in DMAA, THF, bis-2-ethoxyethanol and isobutyl methyl ketone. Strong transparent films were prepared by casting from solutions or compression of these APE devoid of carbonyl, sulfonyl, nitrile and other polar groups. Such films have low DC ($\varepsilon \leqslant 2.8$) and moisture absorptivity ($\leqslant 0.1\%$) and are distinguished by high thermal stability and mechanical strength. Figure 3 gives the dependence of ε on r for APE **7a** as an example.

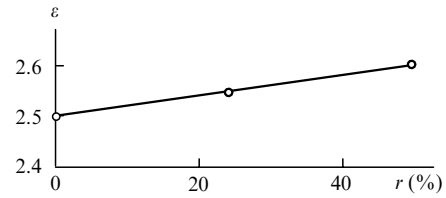


Figure 3. Dependence of dielectric constant on relative humidity for APE **7a**.[40]

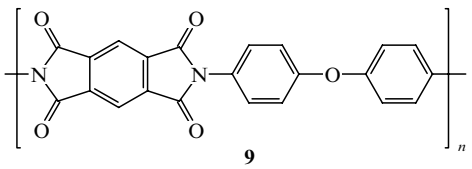
Fluorinated APE were used to prepare the family of FLARE polymers with low values of ε and moisture absorptivity. For example, the values of ε for FLARE^{TM} 1.0 and FLARE^{TM} 1.51 are 2.43 and 2.52 and the coefficients of thermal expansion are 73 and 33 ppm (°C)$^{-1}$, respectively.[45]

Fluorine-containing polyimides have also attracted the attention of researchers. A drawback of the systems based on polyimides as regards manufacture of materials with low DC is the presence of four carbonyl groups in each repeating unit. However, the possibility to modify their structures (including fluorination) over wide limits in combination with high thermal stability and mechanical strength make polyimides rather attractive materials for this purpose. Polyimides used in electronics have $\varepsilon = 2.9-3.4$. The decrease in DC is achieved by the introduction of fluorine atoms [5–8, 22, 46–84] into the macromolecules, most often in the form of HFPG [5–8, 11–16, 61, 63, 80, 81, 83] and trifluoromethyl substituents.[74–79, 82, 83]

Synthesis of fluorinated polyimides is performed mainly with the use of dianhydride **2**. This is determined by a relative accessibility of this monomer and by low DC of polymers based on it compared to analogous polymers based on other dianhydrides (see below).

The reaction of **2** with various fluorinated diamines was carried out according to Scheme 5.[21, 22, 63]

Moisture absorptivity and DC values of the polyimides obtained are listed in Table 5. For comparison, the table also contains the corresponding characteristics of poly(diphenylene oxide pyromellitimide) **9**, which is most widely used in microelectronics as an insulator.[85]

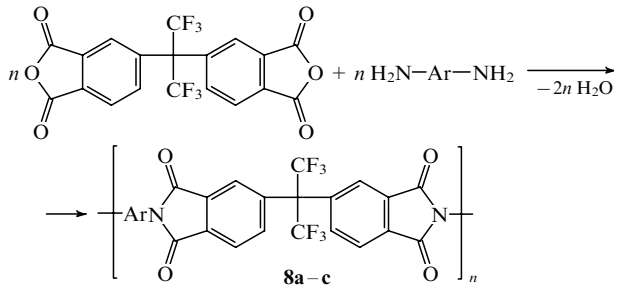


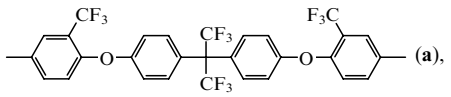
9

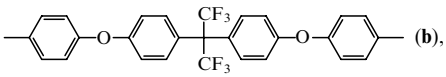
Table 5. Fluorine content, moisture absorptivity and DC of polyimides **8** and **9**.

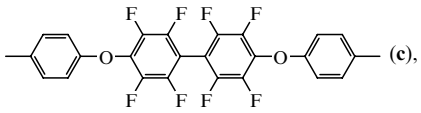
Polymer	[F] (%)	Moisture absorption (%)	ε		Ref.
			r = 0	humid medium	
8a	32.0	0.79	2.71	3.04 (r = 56.8%)	22, 30
8b	24.6	0.85	2.72	3.02 (r = 56.8%)	22, 30
				2.96 (r = 50.0%)	63
8c	28.9	0.71	2.74	2.99 (r = 54.5%)	22, 30
				2.78 (r = 50.0%)	63
9	0	2.77	3.10	3.71 (r = 58.2%)	22, 30

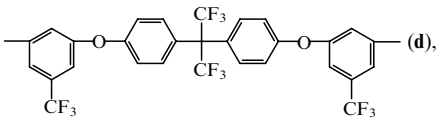
Scheme 5

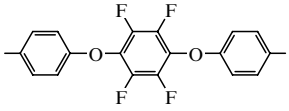


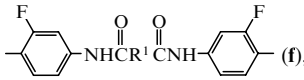
Ar =  (**a**),

 (**b**),

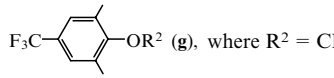
 (**c**),

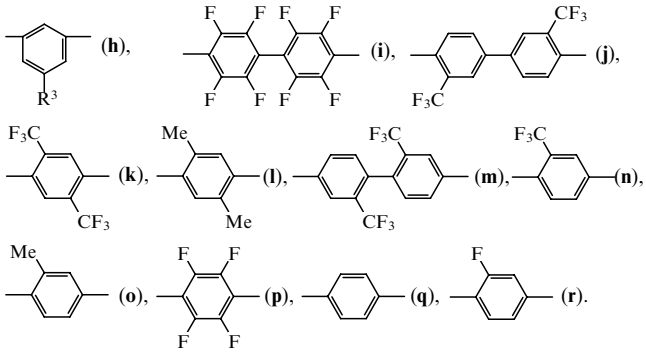
 (**d**),

 (**e**),

 (**f**),

$R^1 = CF(CF_3)[OCF(CF_3)]_mO(CF_2)_5O[CF(CF_3)CF_2]_nCF(CF_3)$ $(m + n = 3)$;

 (**g**), where $R^2 = CH(C_6F_5)_2$, $CH_2(CF_2)_2CF_3$;



It is seen that the parameters of polyimides based on **2** are superior to those of fluorine-free polyimide **9**. For polyimides **8**, the structure of diamines affects little the moisture absorptivity, DC and changes in DC depending on the relative humidity; however, at $r = 0$ the most attractive seems to be the polymer **8a** for which $\varepsilon = 2.71$. The isomeric polyimide **8d** possesses identical properties.[83]

Fluorinated diamines were used in polycondensation with **2**[63] to yield polyimides with high content of fluorine. Dielectric properties of the polyimides **8e**–**g** are presented in Table 6.

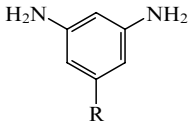
For all the polyimides, the largest ε values in the temperature range studied were found to be at 300 °C, which is due to the increased mobility of polyimide molecules at this temperature exceeding the T_g of the polymers under consideration.

Table 6. Fluorine content and DC of fluorine-containing polyimides **8e**–**g**.[63]

Polyimide	[F] (%)	ε (v = 100 kHz, r = 50%)			
		25 °C	100 °C	250 °C	300 °C
8e	24.61	2.83	2.81	2.89	2.95
8f	48.06	2.93	2.91	2.82	3.00
8g	38.87	2.93	2.98	2.90	3.08

An analogous phenomenon was observed[55] in studies of polyimides based on **2** and octafluorobenzidine. Analysis of the data presented in Table 6 made it possible to conclude that the reduction of ε is more efficient if fluorine atoms are introduced into the aromatic rings of macromolecules rather than into the aliphatic fragments.[63]

The reaction of **2** with fluorine-containing substituted *m*-phenylenediamines



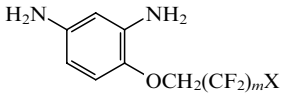
R = SF_5 (**a**), CF_3 (**b**), OCH_2CF_3 (**c**), $CH_2C(CF_3)_2C_3F_7$ (**d**), H (**e**),

yielded polyimides **8h** which are characterised by low values of ε (Table 7) decreasing in the following order R : H > $CH_2C(CF_3)_2C_3F_7$ > OCH_2CF_3 > CF_3 > SF_5.

Table 7. Dielectric constants of polyimides **8h**.

R	ε	v (r = 50%) /kHz	Ref.
SF_5	2.51	10^6	66
CF_3	2.58	10^6	74
OCH_2CF_3	2.60	1	59
$CH_2C(CF_3)_2C_3F_7$	2.70	3×10^3	68
H	3.00	1	59

For polyimides based on **2** and *m*-phenylenediamines containing fluorinated alkoxy substituents,[59, 84]



m = 3, 6, 7, 10; X = H, F,

the values of ε are lower than for polyimides based on **2** and nonsubstituted *m*-phenylenediamine (Fig. 4); with an increase in the fluorine content in these polymers, the value of ε decreases to 2.6.

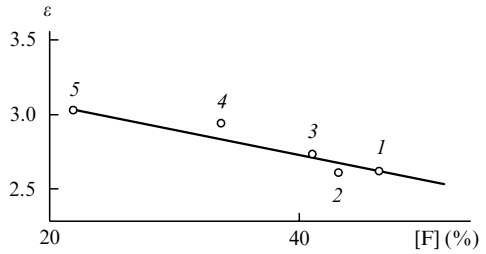


Figure 4. Dependence of dielectric constant (at a frequency of 1 kHz) on the fluorine content in polyimides of general formula **8b**.
R: (*1*) $OCH_2(CF_2)_{10}H$; (*2*) $OCH_2(CF_2)_7F$; (*3*) $OCH_2(CF_2)_6F$; (*4*) $OCH_2(CF_2)_3F$; (*5*) H.

These results may be explained by a decrease in the interchain interactions in polyimides;[50] an increase in the length of the fluorinated alkoxy group leads to a steric hindering of the interchain interaction, which, in turn, decreases ε.

Introduction of fluorinated alkoxy groups is related to two opposite aspects of the influence of fluorine atoms on DC. On the one hand, fluorine has low electronic polarisability,[86] due to which DC of a polyimide is reduced. On the other hand, considerable electron affinity determined by the high electronegativity of fluorine atoms[87] favours the appearance of additional permanent dipoles on the methylene fragments of the fluorinated alkoxy groups and/or the benzene rings linked with the fluorinated alkoxy groups. These dipoles increase the orientational polarisation and DC. In polyimides, the contribution of these additional permanent dipoles to DC is smaller compared to those of interchain interactions and electronic polarisation.[86]

The reduced water and moisture absorptivity of fluorinated polyimides determines the stability of their dielectric characteristics. Thus after the films have been stored for 5 days at 25 °C and $r = 70\%$, the increase in ε was 0.1 (from 2.6 to 2.7) for the polymer **8h** [R = $CH_2C(CF_3)_2C_3F_7$] (see Table 7), which indicates that water absorptivity considerably influences the DC of the polymers.[59] It should be noted that the stability of the DC is one of the most important properties that should be inherent in ILD used in microelectronics.[87]

A detailed investigation of the relationship between the structure of polyimides and their DC has been undertaken.[7,8] Polyimides **8i**–**r** were obtained based on dianhydride **2** and different diamines with or without fluorine atoms in the benzene rings and side groups.

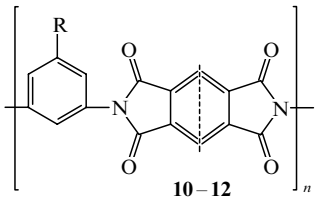
The values of ε for these polyimides are listed in Table 8. Under all measurement conditions the same trend was observed, *viz*., a decrease in DC of polyimides with the increase in fluorine content in these polymers. Some deviations from this trend are determined, in particular, by the fact that the methyl-containing polymers with low fluorine content are partially aliphatic, which diminishes the DC.[7] It should also be noted that an asymmetrical arrangement of fluorinated fragments in the amine residues leads to an increase in the DC of polyimides with the same number of fluorinated fragments arranged symmetrically.[7] An analysis of the results presented in Table 8 shows that the DC of polyimides decreases in the following order: **8r** > **8q** > **8o** > **8p** > **8n** > **8l** > **8m** > **8k** > **8i**.

Table 8. Dielectric constants of polyimides **8i**–**r**.

Polyimide	ε (1 kHz)	
	$r = 0$	$r = 40\%$
8i	2.55	2.73
8j	2.56	–
8k	2.59	2.87
8l	2.68	2.90
8m	2.71	2.89
8n	2.72	3.05
8o	2.74	3.21
8p	2.75	3.16
8q	2.81	3.22
8r	2.85	3.19

The effect of the dianhydride structure on the properties of polyimides has been investigated[59,66,68,74] in studies of physical properties (including DC) of polyimides of general formulae **10**–**12**. The results obtained are presented in Table 9. According to these data, the magnitude of ε decreases in the following order: **10e** > **10d** > **10c** > **10b** > **10a**.

Analysis of the properties of polyimides of general formula **11** revealed a different dependence.[66]



10–**12**

R = CF_3 (**10**), SF_5 (**11**), $CH_2C(CF_3)_3$ (**12**).

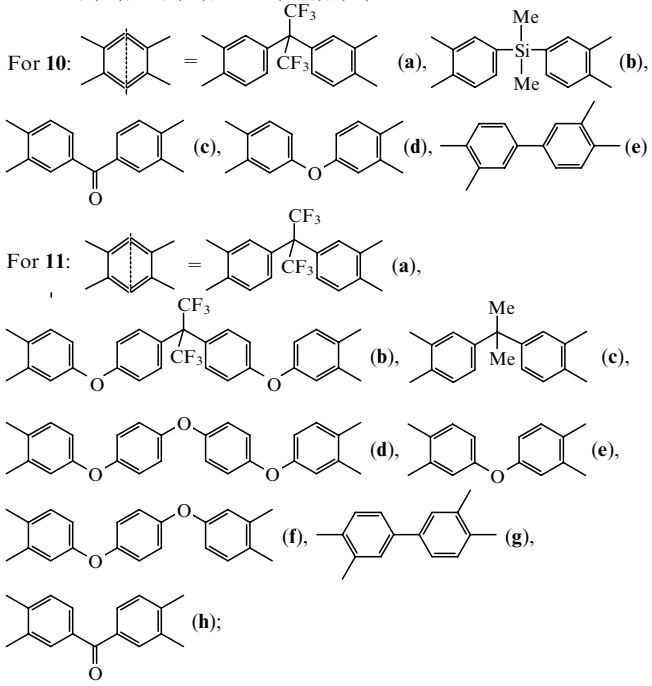


Table 9. Specific viscosity (η_{log}), glass transition temperature and DC of polyimides **10.**

Polyimide	η_{log} /dl g^{-1}	T_g /°C	ε (10 GHz)
10a	0.70	297	2.58
10b	0.64	263	2.75
10c	0.53	294	2.90
10d	0.34	274	2.91
10e	0.89	329	3.02

Note. Polyimides **10a**–**10d** are soluble in DMAA and *m*-cresol; films can be prepared from solutions of polyimides **10a**, **10c**–**10e** in *m*-cresol and DMAA.

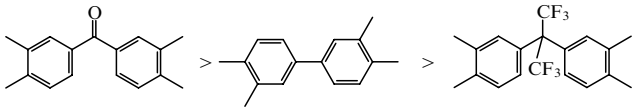
Some characteristics of these polymers are presented in Table 10. It is seen that values of ε decrease in the order: **11h** = **11g** > **11f** > **11e** > **11d** > **11c** > **11b** > **11a**. The values of ε for SF_5-containing polyimides presented in Table 10 are rather low: at a frequency of 10 GHz they vary from 2.51 to 3.00, *i.e*., they are about 0.2 unit lower than those for the corresponding polymers based on *m*-phenylenediamine.

Table 10. Specific viscosity, glass transition temperature, temperature of 10%-mass loss (DTGA) and DC of SF_5-containing polyimides **11**.

Polyimide	η_{log} /dl g^{-1}	T_g /°C	$T_{10\%}$ /°C	ε (ν = 10 GHz)
11a	0.35	305	476	2.51
11b	0.44	243	480	2.61
11c	0.38	300	426	2.68
11d	0.45	235	457	2.80
11e	0.48	287	470	2.82
11f	0.40	263	471	2.83
11g	0.44	344	471	3.00
11h	0.40	308	461	3.00

Similar polyimides with pentafluorosulfanyl (Table 10) and trifluoromethyl (Table 9) substituents, have close ε values; sometimes the former are characterised by lower ε values, which is related to a higher fluorine content in these systems.

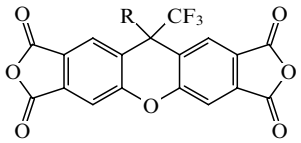
For the polyimides based on *m*-phenylenediamines with fluorinated alkoxy groups, the ε values decrease in the series of dianhydrides:[59]



Of all of the analysed polyimides, those based on dianhydride **2** and containing the bulky hexafluoropropane-2,2-diyl have the lowest ε values compared to polyimides derived from other tetracarboxylic acid dianhydrides. It is the dianhydride **2** that served as the basis for manufacture of polyimide films with $\varepsilon < 3.0$ (for the Hoechst Sixef film, $\varepsilon = 2.6$) and low ($\sim 0.5\%$) water absorptivity.[61]

In later studies,[67,88–90] it was shown that a considerably better combination of mechanical and electrical properties can be reached by introducing fluorine-containing groups into rigid 'rod-like' monomers; films of such polymers have low thermal expansions typical of metals and ceramics.[91–93]

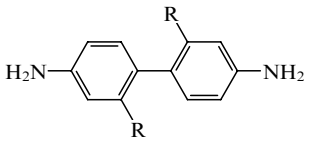
Xanthene-2,3,6,7-tetracarboxylic acid dianhydrides were used for the preparation of rigid-chain fluorinated polyimides (see Refs 94, 95)



R = CF_3 (**a**), Ph (**b**).

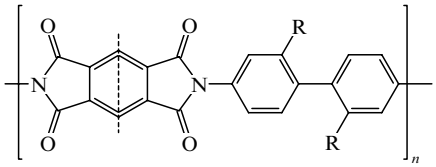
The reaction of these dianhydrides with a number of the above-mentioned fluorinated diimines yielded polyimides **12**, which are characterised by low ε values (lower than in polyimides based on **2**), low coefficients of thermal expansion and good solubility in organic solvents simultaneously. The properties of this type of polyimides are listed in Table 11.[68]

Polyimides with even lower thermal expansion coefficients were obtained by the reaction of xanthene-2-3,5,6-tetracarboxylic acid dianhydrides with 'rigid' fluorinated aromatic diamines, *viz.*, bis(fluoroalkyl)- and bis(fluoroalkoxy)benzidines:



R = CF_3, OCF_3, OCF_2CF_2H.

The rigid-chain polyimides obtained had the following formula



13a,**b**

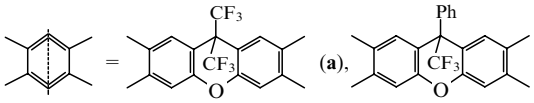


Table 11. Film thickness (d), tensile strength (σ), tensile elongation (Δl), elasticity modulus (η), thermal expansion coefficient (α), moisture absorptivity and DC for films based on fluorine-containing polyimides **12**.[68]

Polyimide	d /μm	σ /MPa	Δl (%)	η /GPa	α /ppm (°C)$^{-1}$	Moisture absorption (%) (r = 85%)	ε (1 MHz, r = 0)
12a	10.5	116	28	2.0	70	0.6	2.3
12b	13.6	115	25	1.9	67	1.1	2.5
12c	14.6	72	6	1.7	86	0.5	2.7

Some characteristics of such fluorinated polyimides are listed in Table 12.[69,70]

Table 12. Fluorine content, tensile strength (σ), tensile elongation (Δl), elasticity modulus (η), thermal expansion coefficient (α), moisture absorptivity and DC for fluorine-containing polyimides **13**.[69]

R	[F] (%)	σ /MPa	Δl (%)	η /GPa	α /ppm × ×(°C)$^{-1}$	Moisture absorption (%) (r = 85%)	ε (ν = 1 MHz, r = 0)
Polyimide **13a**							
CF_3	30.7	200	6	6.1	6	1.2	2.4
						1.4	2.7
OCF_3	29.4	411	18	5.1	10	0.8	2.8
$O(CF_2)_2H$	31.7	294	15	5.3	10	0.7	3.0
Polyimide **13b**							
CF_3	22.8	197	8	5.0	6.2	1.9	2.7
OCF_3	21.8	143	7	3.4	36	–	2.6
$O(CF_2)_2H$	24.77	249	19	4.0	40	0.8	3.1

Polymers based on diamine with the OCF_3 substituents are characterised by small values of ε, low moisture absorptivities and low thermal expansion coefficients and, at the same time, possess high thermal stability. Such polymers are rather promising as the next-generation materials for microelectronics.

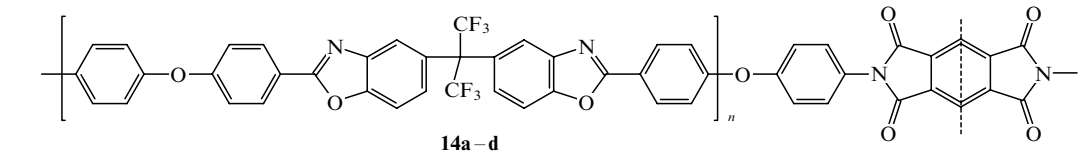
Along with fluorinated APE and polyimides, other types of fluorinated aromatic polymers were also used for the production of low-DC materials. Polybenzooxazoles (PBO) **14** are typical representatives of such polymers (Scheme 6).[96–98]

Despite the fact that introduction of benzooxazole units into macromolecules of polyimides did not result in a decrease in DC

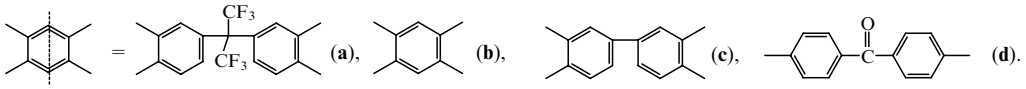
Table 13. Dielectric constants of polyimides **14**.[99]

Polyimide	ε	
	r = 0	r = 70%
14a	2.88	3.70
14b	3.01	4.29
14c	3.21	4.80
14d	3.21	4.45

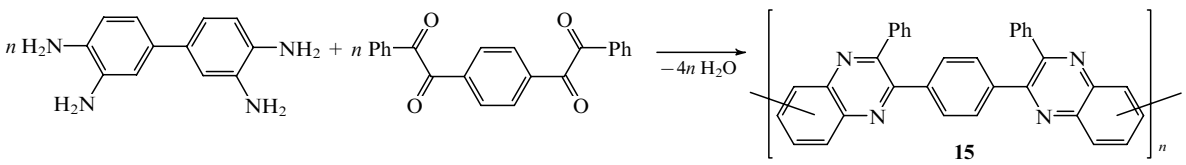
Scheme 6



14a–d



Scheme 7



15

of the latter (Table 13),[99] highly fluorinated PBO [100, 101] appear to be rather promising polymers for the creation of materials with low DC. In any case, for some fluorinated PBO in the humid state $\varepsilon = 2.8$ (see Refs 102, 103), and a PBO with $\varepsilon = 2.2-2.4$ has been reported.[104]

Yet another promising class of heterocyclic polymers are polyphenylquinoxalines (PPQ).[105–107] The information about dielectric properties of PPQ is rather limited,[1, 108] but the fact that even a fluorine-free PPQ obtained by Scheme 7 has (depending on the temperature and measurement frequency) $\varepsilon = 2.70-3.05$ (see Table 14) allows optimistic conclusions about DC of fluorinated PPQ. At present, there are real possibilities for the preparation of PPQ containing fluorine in both the phenyl groups[109] and the hexafluoropropane-2,2-diyl 'bridges'.[110]

Table 14. Temperature of measurement, frequency and DC of PPQ of general formula **15**.[1]

T /°C	ν /kHz	ε
45	2×10^1	2.86
45	2×10^3	2.70
100	2×10^1	3.05
100	2×10^3	2.82

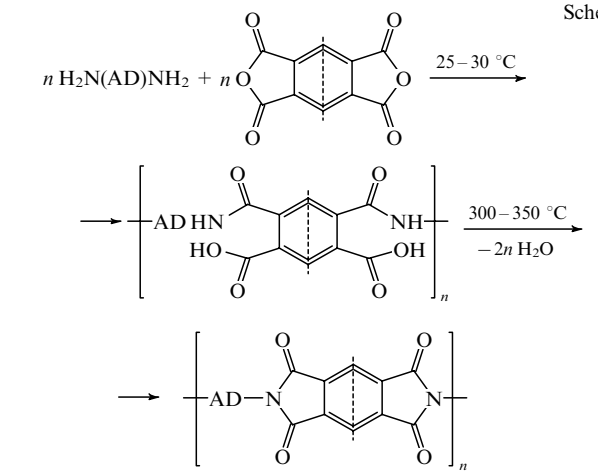
2. Polymers with alicyclic units

In the case of fluorinated polymers, a possibility exists of HF evolution in the course of their processing; therefore, in recent years ever-growing attention is paid to fluorine-free CP containing alicyclic fragments (ACF). The most popular ACF is adamantane and its derivatives.[111] In particular, adamantane-containing diamines used as starting compounds in the synthesis of polyimides have been described.[112–116] Polyimides were synthesised by a two-step procedure consisting of low-temperature reaction of adamantane-containing diamines with tetracarboxylic acid dianhydrides and subsequent solid-phase thermal treatment of the resulting polyamido acids (Scheme 8).

Along with the two-step procedure for the synthesis of polyimides, a one-step high-temperature (200 °C) polycyclocondensation in *m*-cresol with isoquinoline as the catalyst can also be used to this end. As a rule, this yields higher-molecular-weight polyimides.

After incorporation of adamantane-containing fragments, the solubility of some polyimides in organic solvents is enhanced, they are less coloured than the aromatic polyimides and their DC values are diminished. The lowest ε values are characteristic of polyimides based on 4,9-bis[4-(4-aminophenoxy)phenyl]diada-

Scheme 8



16

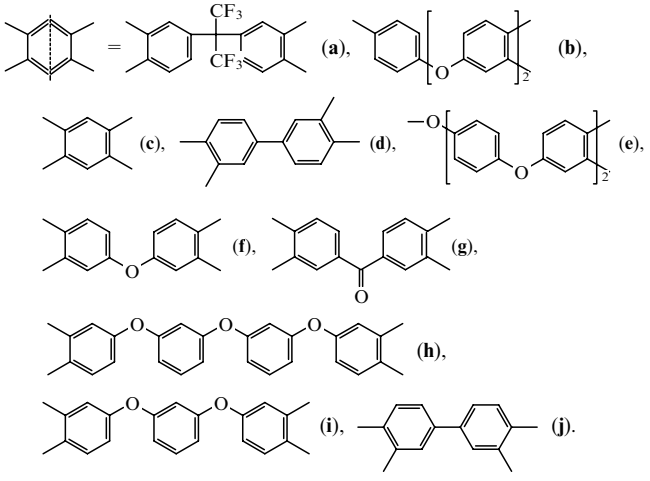


Table 15. Specific viscosity (30 °C, *N*-methylpyrrolidone), glass transition temperature, thermal expansion coefficient, moisture absorptivity and DC of polyimides **16**.[114]

Polyimid	η_{log} /dl g^{-1}	T_g /°C (DSC)	α /ppm (°C)$^{-1}$	Moisture absorption (r = 85%)	ε (ν = 1 kHz, r = 0)
16a	0.63	349	57.5	0.122	2.58
16b	0.43	292	67.1	0.149	2.65
16c	–	394	67.8	0.133	2.66
16d	–	–	72.4	0.149	2.66
16e	0.80	267	74.9	0.163	2.67
16f	0.52	319	56.5	0.137	2.69
16g	–	341	41.6	0.264	2.74

mantane of the general formula **6**.[114] Some characteristics of these polyimides are listed in Table 15.

Along with the synthesis of polyimides, the diadamantane-containing monomers were also used for the synthesis of polybenzoazoles.[117]

IV. Thermostable polymeric foams

An alternative to the above approaches to the creation of polymeric materials with low DC is the use of thermostable polymeric foams.[1, 118–132] Polymeric foams were prepared from microphase-separated block- or graft-copolymers composed of thermostable and thermolabile blocks, the latter forming the dispersed phase.[1] The thermally degradable block should be a functional oligomer of a strictly determined structure; furthermore, it should undergo quantitative disintegration into non-reactive species that diffuse easily through a glassy polymeric matrix. The temperature of destruction of unstable blocks must be sufficiently high to allow preparation of standard films with the removal of a solvent; at the same time, it must be considerably lower than the glass transition temperature of the polyimide block in order to avoid foam degradation.[121] Hence, the difference between the temperature of unstable block destruction and the glass transition temperature of the polymeric matrix determines the 'processability window' of the material. Upon heating, the thermally unstable blocks undergo degradation to produce pores, the size and shape of which are determined by the morphology of the initial copolymers.

This type of foams having pores of about 1 nm in size are called nanofoams.[1] A decrease in DC is achieved by replacing part of a polymer with ε = 3.2 by air with ε = 1 (see Ref. 1).

The choice of different polyimides,[118–130] PPQ [1] or PBO,[131] as thermostable polymeric matrices is determined by their high thermal stability together with solubility (at least, at the prepolymer stage) in organic solvents.

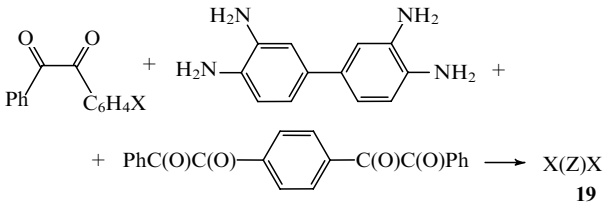
The following polymers are most often used as thermolabile blocks: poly(propylene oxide) (PPO),[1, 118–122, 124, 125, 128, 129, 131] poly(methyl methacrylate) (PMMA),[1, 124] polystyrene,[123, 125] poly-α-methylstyrene [123, 125, 127] and aliphatic polyethers.[126]

Examples of such systems are amorphous polyimides based on a card diamine, 9,9-bis(4-aminophenyl)fluorene, with the terminal (**17**) or lateral (**18**) PPO blocks (Scheme 9).[118, 121]

In the synthesis of polyimides **17a**,**b** the second amine component was PPO *p*-aminobenzoate; in the case of **18a**,**b** part of the card diamine was replaced by PPO 3,5-diaminobenzoate. Films of soluble polymers **17a** and **18a** were obtained from solution, whereas films of insoluble polymers **17b** and **18b** were prepared in the stage of soluble polyamido acids with subsequent thermal cyclisation. Conditions of this stage (300 °C, 5–10 h) allowed formation of foams of both polyamide **17** and polyamide **18**.

The density of the polymers points clearly to the formation of intumescent structures: the density of matrix polyimides is 1.28 g cm^{-3}, while those of nanofoams range from 1.09 to 1.27 g cm^{-3} (see Ref. 121). Thus, the volume fraction of pores makes up from 15% to 1%.

Nanofoams based on copolymers of PPQ (matrix) and PPO or PMMA (terminal blocks) were prepared using for their synthesis the monomer–oligomer approach according to the following scheme:

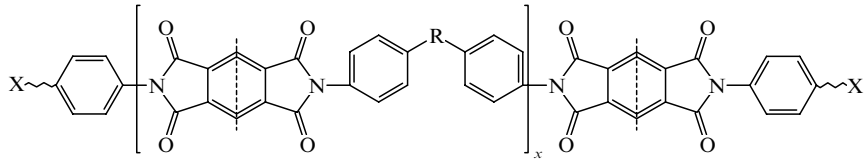


19

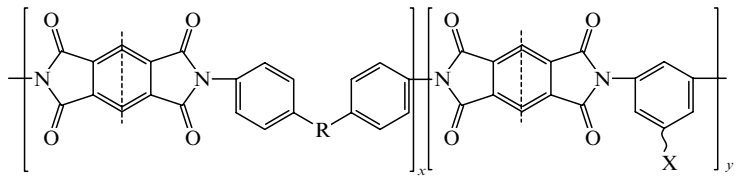
X = PPO (**a**), PMMA (**b**); Z = PPQ.

In order to induce destruction of terminal blocks, films of copolymers **19a**, **b** were heated in air for 9 h at 275 °C and for 5 h at 340 °C, respectively. The density of intumescent polymers reached 1.16–1.19 g cm^{-3}, which is appreciably lower than the density of a PPQ homopolymer (1.32 g cm^{-3}). Accordingly, 10%–12% of the film volume were voids. Some characteristics of intumescent polymers are listed in Table 16. It is seen that ε decreases from 2.7 for PPQ homopolymer to 2.31 for intumescent copolymers **19a**.

Scheme 9

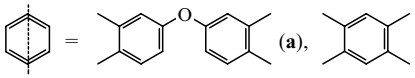


17a–b



18a,b

R = fluorene-9,9-diyl; X = PPO;



= (**a**), (**b**).

Table 16. Density, temperature of measurement, frequency and DC of a PPQ homopolymer and its intumescent copolymers.[1]

ρ /g cm^{-3}	T /°C	ν /kHz	ε
PPQ – PPO copolymer			
1.16	45	20	2.38
	45	2×10^3	2.31
	100	20	2.36
	100	2×10^3	2.31
PPQ – PMMA copolymer			
1.19	45	20	2.55
	45	2×10^3	2.51
	100	20	2.54
	100	2×10^3	2.50
PPQ homopolymer			
1.32	45	20	2.86
	45	2×10^3	2.70
	100	20	3.05
	100	2×10^3	2.82

The results obtained confirm unequivocally the efficiency of this approach to the preparation of materials with low DC.

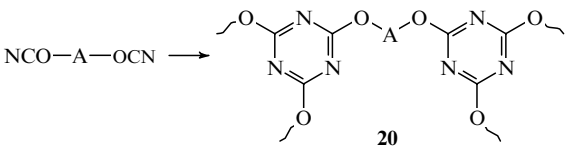
V. Conclusion

The data analysed in this review point to an appreciable progress in the preparation of polymers and polymeric materials with low DC. At present, polyimides meet best the requirements for the dielectric materials employed in microelectronics;[132] however, these requirements are becoming more rigorous, which stimulates further search for new materials.

Computer-assisted analysis of different structures of polymers has shown [133] that considerable progress may be expected if heterochain and heterocyclic polymers are replaced by phenyl-substituted polyphenylenes devoid of polar groups such as C=O, C=N, *etc*. present in polyheteroarylenes.

Polymers of this type were obtained from phenyl-substituted biscyclopentadienones and diethynylarylenes by the Diels – Alder reaction.[134–137] In this case, polyphenylenes with aliphatic [135, 136] and hexafluoropropane-1,2-diyl [137] groups were obtained along with the simplest systems containing only aromatic rings.[134] Apparently, polymeric materials with $\varepsilon = 2.50 - 2.60$ will be prepared based on various modifications of these systems.

Yet another promising direction of studies aimed at the creation of low-DC materials appears to be synthesis of 'cross-linked' polycyclotrimers of fluorinated cyano esters **20**.[138–142] These polymers, obtained according to the scheme,[140]



20

A = $CH_2(CF_2)_nCH_2$; n = 3, 4, 6, 10,

are reported [140] to have the record DC values for homogeneous systems ($\varepsilon \simeq 2.27$). Taking into account the efficiency of the approach to the preparation of nanofoams, it may be expected that materials with uniquely low DC will be obtained based on **20**. The same object is pursued by studies in the field of maleimides, norbornenes, benzocyclobutenes and propargylic compounds.[143–147]

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