

# NEW PHENYL-SUBSTITUTED POLYPHENYLENES WITH A NANOPOROUS STRUCTURE AND ULTRALOW DIELECTRIC CONSTANTS FORMED IN SUPERCRITICAL CARBON DIOXIDE

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## INTRODUCTION

In the context of the ever-increasing demand for design and miniaturization of microchips, development of polymers with ultralow dielectric constant in combination with high thermal and mechanical characteristics becomes of importance [1, 2]. Currently, fluorinated polyimides (dielectric constant  $k = 2.6-2.8$ ) best meet the requirements for polymeric dielectrics [3, 4]. However, the requirements for them become tougher, so that next-generation materials should have  $k < 2$ , which stimulates the search for polymeric materials with ultralow dielectric constants [5].

One approach to the design of polymeric materials with ultralow  $k$  values implies the use of heat-resistant polymeric micro- and nanoporous structures. The latter are usually obtained by decomposition of block copolymers consisting of thermally stable and unstable blocks [6], as well as by thermolysis of polymer blends with high  $T_g$  values and thermally unstable fillers [7]. However, such approaches are rather laborious and are accompanied by undesirable side effects. We have suggested a more efficient, simple and environmentally safe method of nanoporous polymeric structures producing with the use of supercritical carbon dioxide (SC CO<sub>2</sub>). As distinct from the other methods, the method of nanoporous structures preparation in SC CO<sub>2</sub> makes it possible to approach the lowest possible  $k$  value by choosing an appropriate molecular structure and controlling the pore size in the matrix of nanoporous polymeric materials.

## RESULTS

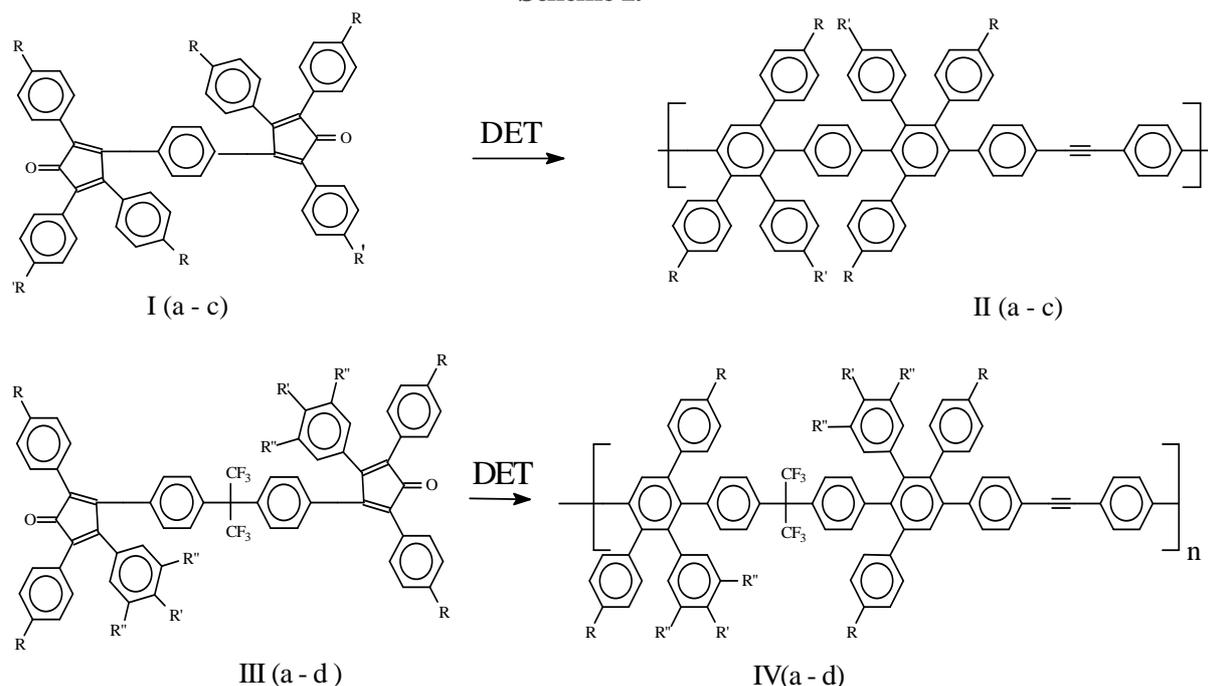
In this work, we synthesized new phenyl-substituted polyphenylenes and obtained, on their basis with the use of SC CO<sub>2</sub>, nanoporous materials with ultralow dielectric constant ( $k < 2$ ) in combination with high thermal and mechanical characteristics. The dielectric properties of the polymeric materials were improved in two steps by (i) synthesizing of fluorinated phenyl-substituted polyphenylenes (FPSPPs) since they have lower dielectric constants ( $k \sim 2.5$ ) [8-10] than common heat-resistant polymers ( $k > 3$ ) and (ii) creating of micro- and nanoporous structures in the FPSPP matrix in SC CO<sub>2</sub>.

Therefore, in this work, using previously synthesized fluorine-containing bis(tetraarylcyclopentadienones) I and III [11], we synthesized new FPSPPs containing fluorine in the central hexafluoroisopropylidene groups and in phenyl rings by the Diels – Alder reaction of compounds I and III with 4,4'-diethynyltolane (DET) (Scheme 1).

FPSPPs were synthesized in 1, 2, 4-trichlorobenzene at 150°C for 40 min. All reactions were homogeneous with nearly quantitative yields. The viscosities were within 0.51-0.85 dL

/ g. The molecular weights and polydispersity of the polymers determined by GPC were within the following ranges:  $M_w = (86.7-120.0) \times 10^3$ ,  $M_n = (30.1-50.4) \times 10^3$ , and  $M_w/M_n = 1.98-2.88$ . The FPSPP structure was confirmed by IR spectroscopy and  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{19}\text{F}$  NMR. The IR spectra of all polymers have no signs of absorption bands of ethynyl ( $3210, 2200 \text{ cm}^{-1}$ ) and carbonyl ( $1709 \text{ cm}^{-1}$ ) fragments of tetraphenylcyclopentadienones, which is evidence of the formation of a polymer and a low concentration of terminal groups. The  $^{13}\text{C}$  NMR spectra do not show the signals at  $\delta = 200$  and  $80 \text{ ppm}$  typical of the cyclopentadienone and terminal acetylene groups. The  $^{19}\text{F}$  NMR spectra of polymers IIa-IIc show the signal at  $\delta = -112 \text{ ppm}$  assigned to the fluorophenyl substituents of the polymers.

**Scheme 1.**



*Ia:* ( $R = R' = H$ , *Ib:*  $R = H$ ,  $R' = F$ ; *Ic:*  $R = F$ ,  $R' = H$ ).

*IIa:*  $R = R' = H$ , *IIb:*  $R = H$ ,  $R' = F$ ; *IIc:*  $R = F$ ,  $R' = H$ ).

*IIIa:*  $R = R' = R'' = H$ , *IIIb:*  $R = R'' = H$ ,  $R' = F$ ; *IIIc:*  $R'' = R' = H$ ,  $R = F$ ; *IIId:*  $R'' = H$ ,  $R' = R = F'$ .

*IVa:*  $R = R' = R'' = H$ , *IVb:*  $R = R'' = H$ ,  $R' = F$ ; *IVc:*  $R'' = R' = H$ ,  $R = F$ ; *IVd:*  $R'' = H$ ,  $R' = R = F$ ).

All synthesized polymers are soluble in common organic solvents: toluene, THF, DMSO, DMF, N-MP, and chloroform. The high solubility of the polymers in chloroform allowed us to obtain their films with a tensile strength ( $\sigma$ ) of 58.8-69.5 MPa and an elongation ( $\epsilon$ ) of 3.1-8.1% (Table 1).

**Table 1.** Some molecular weight, thermal, and mechanical characteristics of FPSPPs II and IV

Polymer	$\eta_{\text{red}}$ , dL/g (N-MP, 25°C)	$M_w \cdot 10^3$	$M_n \times 10^3$	$M_w/M_n$	$T_{10}^\circ\text{C}$		Tensile properties of films	
					air	argon	$\sigma$ , MPa	$\epsilon$ , %
IIa	0.78	99.8	50.4	1.98	470	510	67.0	5.0
IIb	0.85	101.4	48.3	2.10	477	521	69.5	5.4
IIc	0.65	110.0	46.3	2.38	460	515	65.0	5.0
IVa	0.64	112.5	45.0	2.50	473	513	65.8	8.1

IVb	0.59	110.1	39.3	2.80	449	501	66.1	7.8
IVc	0.70	120.0	50.0	2.40	476	520	63.2	7.0
IVd	0.51	86.7	30.1	2.88	417	500	58.8	3.1

FPSPPs have high glass transition temperatures (290-340°C, Table 2). The temperature of 10% weight loss for all polymers in an argon atmosphere and in air was in the range 501-521 and 417-477°C, respectively. The  $k$  values for dense fluorinated polymers measured in vacuum at a frequency of 1 kHz were within 2.54-2.74. As expected, the introduction of fluorine into macromolecules of phenyl-substituted polyphenylenes (PSPPs) was accompanied by a decrease in the dielectric constants of these systems as compared with the previously synthesized nonfluorinated PSPPs [8]. This is likely due to the substitution of hydrogen atom for bulky fluorine atom in PSPPs leading to a decrease in the electronic polarizability of the C-F bond as compared with that of the C-H bond, the decrease in the chain packing density, and the increase in the free volume and hydrophobicity of the polymer.

On the basis of the FPSPPs, micro- and nanofoams with controlled pore size and shape were obtained. First, polymer films were saturated with carbon dioxide at the saturation pressure  $P_{\text{sat}} = 5$  MPa and the saturation temperature 7-25°C. After CO<sub>2</sub> was sharply removed from the reactor (5 s), the film was dipped for 30 s (foaming time) into a glycerol bath heated to  $T_{\text{foam}} = 240$ -290°C. This was accompanied by sharp desorption of CO<sub>2</sub> from the surface and simultaneous foaming of the polymeric material. The surface was depleted of carbon dioxide, and a dense skin layer formed around the foamed core. The foamed samples were placed into an ethanol-water (1:1) mixture and dried in vacuum for 20 h at 30°C. Some characteristics of the foamed polymers are listed in Table 2

**Table 2.** The electrophysical characteristics of FPSPPs II and IV

Sample	$T_{\text{foam}}$ °C	$T_g$ °C	Density, g/cm <sup>3</sup> *	Morphology**	k***
IIa	-	340	1.28	Dense polymer	2.80
	250		1.22	Micropores	2.58
	290		0.98	Nanopores	2.00
IIb	-	330	1.25	Dense polymer	2.74
	250		0.95	Micropores	2.4
	290		0.78	Nanopores	1.77
IIc	-	311	1.24	Dense polymer	2.69
	250		0.91	Micropores	2.18
	290		0.71	Nanopores	1.70
IVa	-	297	1.24	Dense polymer	2.63
	240		1.08	Micropores	1.97
	280		0.86	Nanopores	1.68
IVb	-	290	1.24	Dense polymer	2.58
	240		1.10	Micropores	1.91
	280		0.71	Nanopores	1.65
IVc	-	303	1.24	Dense polymer	2.54
	240		1.02	Micropores	1.88
	280		0.70	Nanopores	1.65
IVd	-	295	1.23	Dense polymer	2.54
	240		0.98	Micropores	1.81
	280		0.73	Nanopores	1.61

Note:  $P_{\text{sat}} = 5$  MPa,  $T_{\text{sat}} = 25^\circ\text{C}$ .

\* *The density of common and foamed polymers was determined according to ASTM-D-792 "Standard Test Methods for Density and Specific Gravity (Relative Density) of Plastics by Displacement" in hexane.*

\*\* *The morphology of foamed polymer samples was studied with a transmission electron microscope.*

\*\*\* *The dielectric constant was measured at 1 kHz and 25°C in a vacuum of 10 mm Hg.*

The morphology of the films mainly depended on variation of  $P_{\text{sat}}$ ,  $T_{\text{sat}}$ , and  $T_{\text{foam}}$ . According to transmission electron microscopy, the porous FPSPP films have cellular morphology with pores 50-100 nm in size. For all polymers at their maximal foaming temperature  $T_{\text{foam}}$ , comparable porosities of ~40% were obtained. The dielectric constants of the nanoporous materials were within 2.74-1.61 depending on the polymer structure and foaming temperature. These  $k$  values are considerably lower than the limiting  $k$  value for common polymers.

In summary, it is worth noting that  $P_{\text{sat}}$ ,  $T_{\text{sat}}$  and  $T_{\text{foam}}$ , as well as the decompression regime, can be used as additional parameters for controlling the pore size. The decrease in  $T_{\text{sat}}$  to zero considerably improves the solubility of  $\text{CO}_2$  and thereby reduces the  $\text{CO}_2$  diffusion rate from the film. Microcellular morphologies prevail when saturation occurs at 25°C, whereas nanoporous morphologies with record low  $k$ 's are formed at  $T_{\text{sat}} = 0$  °C. Only nanoporous structures with a pore size below 10 nm can be potentially used in multilayer integrated circuits [5]. We intend to study the effect of  $T_{\text{sat}}$  and other parameters of the process, as well as the pore size and shape, on the dielectric constant  $k$ .

## CONCLUSION

Thus, we have synthesized new FPSPPs and, on their basis, have developed heat-resistant nanoporous materials with controlled ultralow dielectric constants (1.97-1.61). The approach to the development of nanoporous structures for PSPPs with the use of SC  $\text{CO}_2$  is suggested for the first time and is a base for the creation of new breakthrough technologies in the field of microelectronics.

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