ISSN 0012-5008, Doklady Chemistry, 2010, Vol. 432, Part 2, pp. 159–164. © Pleiades Publishing, Ltd., 2010.
Original Russian Text © M.L. Keshtov, E.I. Mal'tsev, A.M. Lopatin, L.N. Nikitin, I.A. Blagodatskikh, M.N. Buzin, S.M. Pozin, A.R. Khokhlov, 2010, published in Doklady Akademii Nauk, 2010, Vol. 432, No. 4, pp. 490–495.

CHEMISTRY

New Electyroluminescent Phenyl-Subsituted Polyfluorenes Synthesized in Supercritical Carbon Dioxide

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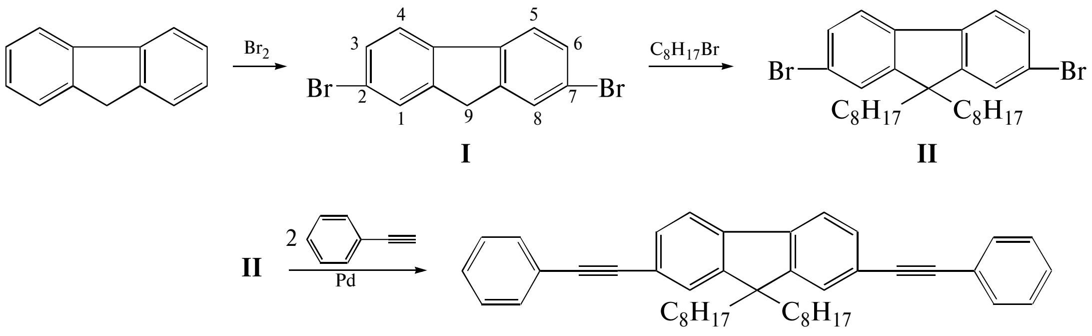
Received January 18, 2010

DOI: 10.1134/S0012500810060029

Blue luminescent polymers have attracted considerable recent attention, both academic and practical, due to their application in full-color displays and green, red, and white LEDs, as well as in design of next-generation light sources [1–4]. Therefore, development of efficient blue luminescent polymers is of importance for such applications.

Among blue electroluminescent polymers, of most interest are polyfluorenes (PFs) and their derivatives, which exhibit high quantum luminescence yields and excellent chemical and thermal stability and photostability [5]. However, they are not free of disadvantages. Alkyl-substituted PFs exhibit poor electroluminescence and low color stability due to polymer chain aggregation, oxidative destruction, and the presence of residual high-boiling solvents and metal catalyst traces. In this context, in this work, we have suggested a new catalyst-free method of synthesis of high-purity electroluminescent polymers based on phenyl-substituted polyfluorenes (PSPFs) in supercritical carbon dioxide. The PSPF synthesis by the Diels–Alder reaction in supercritical carbon dioxide afforded high-purity polymers free of traces of high-boiling solvents and metal catalysts. The presence of a large number of side bulky phenyl substituents made it possible to suppress chain aggregation and improve the solubility and film-forming properties [6, 7].

Bis(triarylcyclopentadienone), a key monomer for PSPF synthesis, was obtained by Scheme 1.



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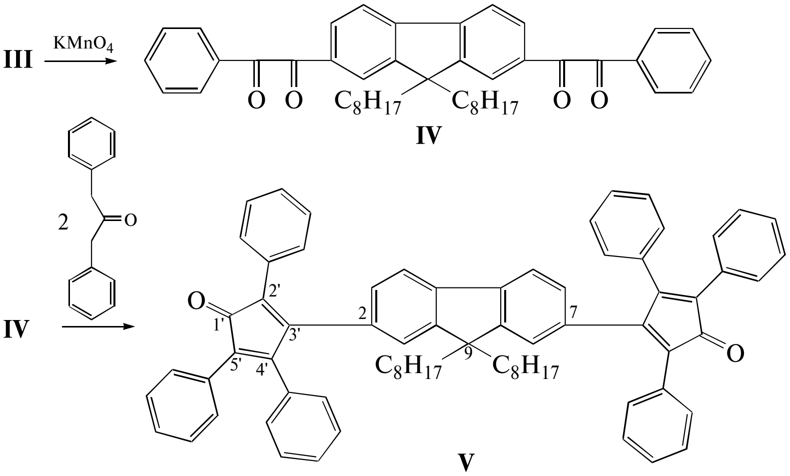


Scheme 1.

At the first stage, fluorine was brominated to give compound **I**, which was then introduced into the reaction with a twofold molar amount of bromooctane. Then, the resulting 2,7-dibromo-9,9-dioctylfluorene (**II**) was cross-coupled with a twofold molar amount of phenylacetylene in the presence of a Pd catalyst. 2,7-Bis(phenylethynyl)-9,9-dioctylfluorene (**III**) thus obtained was oxidized by potassium permanganate to 2,7-bis(phenylglyoxalyl)-9,9-dioctylfluorene (**IV**), which was treated with 1,3-diphenylacetone to produce the target monomer (**V**). Some results of this synthesis (Scheme 1) and study of compounds **I**–**V** are summarized in Table 1. As is seen, the intermediate and target products were obtained in high yields and the elemental analysis data corresponded to the calculated values. The structures of these compounds were confirmed by IR and ^{1}H and ^{13}C NMR spectra (Table 2).

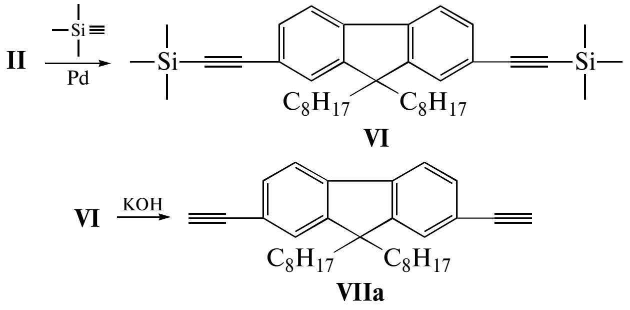
The ^{1}H NMR spectra of bis(cyclopentadienone) **V** are rather complicated. The aromatic protons give rise to downfield multiplets in the δ range 6.80–7.53 ppm (m, 36H), and the signals of the aliphatic protons are observed in the high field in the range 0.25–1.50 ppm (m, 34H). However, the integrated intensity ratio of the aromatic and aliphatic parts corresponds to the suggested structure. In this case, the ^{13}C NMR spectra are more informative. The spectrum of compound **V** shows downfield signals near 200 ppm typical of the

Table 1. Characteristics of compounds **I**–**VII**

Compound	Yield, %	T_m, °C	Empirical formula	Elemental analysis (found/calculated), %		
				C	H	Br
I	93.2	161–163	$C_{13}H_8Br_2$	48.40/48.19	2.22/2.49	49.53/49.32
II	91.2	52–54	$C_{29}H_{40}Br_2$	63.10/63.51	7.39/7.35	29.09/29.14
III	85.2	82–84	$C_{45}H_{50}$	90.55/91.47	9.21/8.53	–
IV	96.8	91–93	$C_{45}H_{50}O_4$	81.24/82.53	7.35/7.70	–
V	95.4	168–170	$C_{75}H_{70}O_2$	90.10/89.77	7.10/7.03	–
VI	94.05	89–91	$C_{39}H_{58}Si_2$	81.13/80.34	10.71/10.03	–
VII	82.2	44–46	$C_{33}H_{42}$	90.21/90.35	7.94/9.65	–

carbonyl group of the cyclopentadienone moiety, and the number of characteristic signals in the aromatic and aliphatic ranges 169–110 and 13–60 ppm, respectively, corresponds to the suggested structure. The structure was also proved by IR spectra. In particular, the IR spectrum of compound **V** shows a band at 1711 cm^{-1} corresponding to stretching vibrations of the carbonyl group.

To obtain PSPFs, we used the simplest bis(acetylene)s *p*-diethynylbenzene and 4,4-diethynyltolane, as well as 2,7-diethynyl-9,9-dioctylfluorene (**VIIa**), synthesized by Scheme 2.



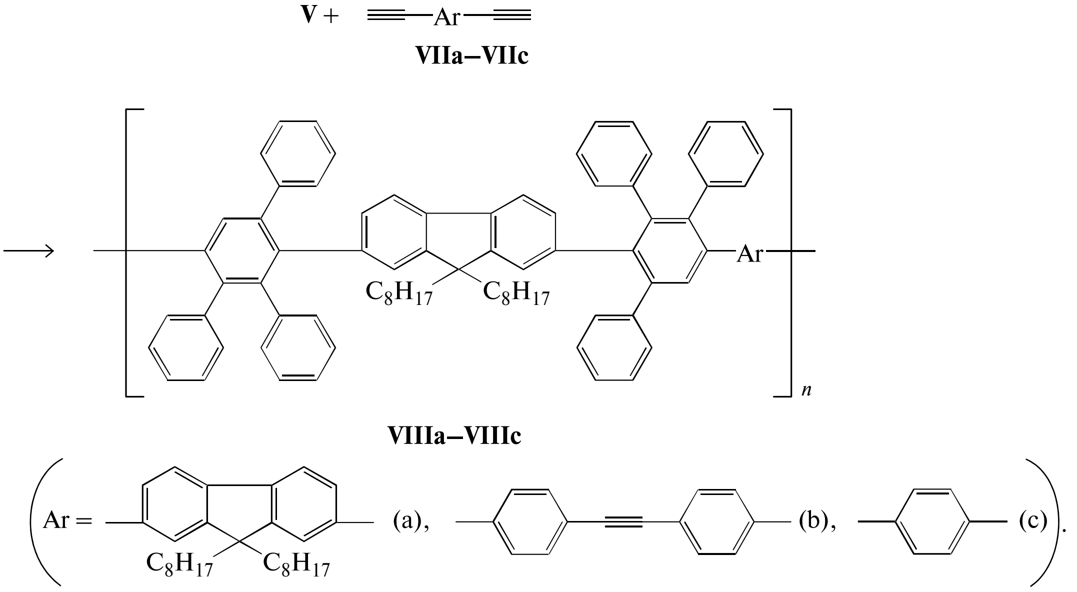
Scheme 2.

2,7-Diethynyl-9,9-dioctylfluorene (**VII**) was synthesized by Pd-catalyzed cross-coupling of 2,7-dibromo-9,9-dioctylfluorene with a twofold molar amount of trimethylsilylacetylene with the subsequent removal of the trimethylsilyl group by treatment with potassium carbonate. The structure of compound **VII** was confirmed by ^1H and ^{13}C NMR and IR spectroscopy. The ^1H NMR spectrum shows two doublets and two singlets at 7.62, 7.47, 7.45, and 3.14 ppm due to the aromatic and terminal ethynyl protons of the fluorene fragment, respectively. The ^{13}C NMR spectrum of compound **VII** shows two signals at 85.50 and 76.98 ppm characteristic of the acetylene moiety. The IR spectrum shows a band at 2107 cm^{-1} characteristic of the C≡C bond.

PSPFs **VIIIa–VIIIc** were synthesized by the reaction of equimolar amounts of bis(cyclopentadienone) **V** with bis(ethynyl)s **VIIa–VIIc** in supercritical carbon dioxide according to Scheme 3. PSPFs were synthesized in supercritical carbon dioxide at 200 bar and 180°C for 10 h. The structure of the polymers was confirmed by IR spectroscopy and ^1H and ^{13}C NMR. Their IR spectra lack the signals typical of the C=O (1711 cm^{-1}) and C≡C (2107 cm^{-1}) groups of the cyclopentadienone and ethynyl moieties, respectively. For all polymers, the ^{13}C NMR signals near 200 and 80 ppm typical of the cyclopentadienone and ethynyl moieties are absent in the ^{13}C NMR spectra. The ^1H NMR spectra are rather complicated; however, the integrated intensity ratio of the aromatic and aliphatic signals is consistent with the suggested structures (see Experimental).

Table 2. Spectral characteristics of compounds **I–VII**

Compound	IR; ν, cm^{-1}	NMR; δ, ppm ($CDCl_3$) ^1H	NMR; δ, ppm ($CDCl_3$) ^{13}C
I	–	7.62 (s, 2H), 7.58 (d, 2H), 7.48 (d, 2H), 3.83 (d, 2H)	151.26, 137.86, 129.23, 126.10, 120.98, 120.00
II	–	7.53 (d, 2H), 7.46 (d, 2H), 7.44 (d, 2H), 1.91 (m, 4H), 1.26–1.05 (m, 20H), 0.83 (t, 6H), 0.58 (m, 4H)	152.44, 138.94, 130.04, 126.07, 121.38, 120.96, 55.56, 40.03, 31.63, 29.78, 29.04, 29.01, 23.53, 22.47, 13.94
III	C≡C 2095 3243	7.34–7.66 (m, 16H), 0.5 (4H, CH_2), 0.71–0.78 (m, 6H, CH_3), 0.9–1.1 (m, 20, CH_2), 1.95–2.05 (m, 4H, CCH_2)	151.0, 140.6, 131.60, 130.71, 128.32, 128.21, 125.92, 123.34, 121.92, 119.90, 90.31, 89.73, 55.21, 40.42, 31.51, 29.73, 23.72, 22.61, 13.92
IV	C=O 1664	7.50–8.05 (m, 16H), 0.5 (4H, CH_2), 0.71–0.78 (m, 6H, CH_3), 0.9–1.10 (m, 20H, CH_2), 1.95–2.05 (m, 4H, CCH_2)	194.40, 193.80, 151.26, 145.51, 135.62, 134.91, 133.22, 130.63, 129.01, 127.11, 123.32, 120.4, 55.91, 40.72, 32.34, 30.87, 29.77, 29.52, 24.10, 22.91, 14.58
V	C=O 1711	6.80–7.53 (m, 36H, Ar), 0.25 (m, 4H, CH_2), 0.82–0.91 (m, 6H, CH_3), 0.95–1.25 (m, 20H, CH_2), 1.42–1.50 (m, 4H, CCH_2)	200.24, 155.23, 154.23, 150.74, 141.00, 133.25, 132.56, 130.97, 130.81, 130.19, 129.36, 128.50, 128.43, 128.09, 128.05, 127.81, 127.53, 127.43, 125.49, 125.30, 123.71, 119.75, 55.05, 40.23, 31.99, 30.03, 29.68, 29.49, 23.73, 22.72, 14.19
VI	C≡C 2149	7.58 (d, 2H), 7.44 (d, 2H), 7.41 (s, 2H), 1.92 (m, 4H), 1.21–1. 0.1 (m, 20H), 0.83 (m, 6H), 0.53 (m, 4H), 0.18 (s, 18H, $SiMe_3$)	150.91, 140.83, 131.20, 126.19, 121.76, 119.79, 106.07, 94.21, 55.21, 40.30, 31.75–22.56 (CH_2), 14.04 (CH_3), 0.17 ($SiMe_3$)
VII	C≡C 2107	7.62 (д, 2H, Ar), 7.47 (d, 2H, Ar), 7.45 (s, 2H, Ar), 3.14 (s, 2H, C≡C), 0.80–1.95 (m, 34H, al)	150.92, 140.87, 131.13, 126.42, 120.70, 119.87, 84.50, 76.98, 55.18, 40.17, 31.73–22.54 (CH), 14.02 (CH_3)



Scheme 3.

The weight-average and number-average molecular weights ($\overline{M}_w$ and $\overline{M}_n$) and polydispersity ($\overline{M}_w/\overline{M}_n$) of the polymers determined by gel permeation chromatography vary within the ranges 5700–11 300, 30 000–51 500, and 3.49–5.26, respectively. All polymers are readily soluble in common organic solvents, such as DMF, THF, *N*-MP, toluene, and chloroform. The thermal and thermooxidative stabilities were estimated by means of DSC and TGA. The stability temperatures of the polymers are rather high and fall within 174–253°C. The exception is polymer **VIIIa**, which is presumably due to the large number of alkyl groups per polymer unit. As follows from Table 3, all PSPFs are highly thermostable. The temperature of 10% weight loss in air and argon is within 350–375 and 400–420°C, respectively.

The figure shows the absorption photoluminescence spectra of the polymers in chloroform. All three luminescence spectra are broad bands, with the long-wavelength edge being shifted into the visible region. According to preliminary data, the observed bands are due to various optical transitions. The nature of each of these bands will be addressed in future studies. However, we can assume that the long-wavelength band is most likely caused by interchain exciplex interaction in the system. In addition, of special interest is the electroluminescent properties of all three polymer structures since organic LEDs with a broad visible emission band are intensively studied with the aim of using them in design of next-generation light sources.

EXPERIMENTAL

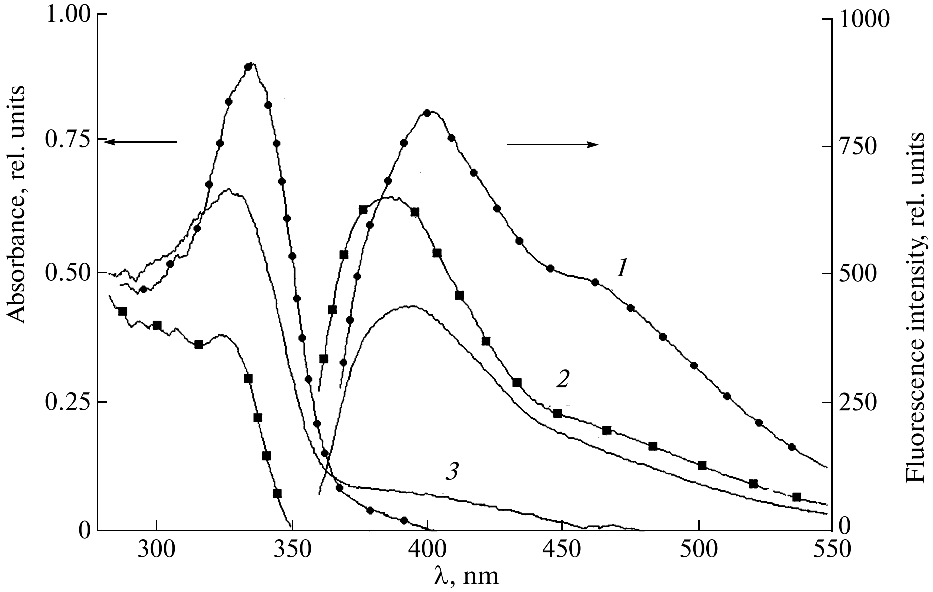
The ^1H and ^{13}C NMR spectra of the compounds and polymers were recorded on a Bruker AMX-400 spectrometer at a working frequency of 400.13 and 100.62 MHz, respectively. The IR spectra were recorded on a Perkin-Elmer 1720-X FTIR spectrophotometer. TGA and DSC were performed on Perkin-Elmer TGA-7 and DSC-7 instruments, respectively, at a heating rate of 10 K/min. Electronic absorption spectra were recorded on a PC-200 spectrophotometer and the fluorescence spectra, on a Hitachi 850 spectrofluorimeter.

Synthesis of Initial Compounds

2,7-Dibromofluorene (I). A solution of bromine (62.6 g, 392 mmol) in chloroform (40 mL) was introduced dropwise over a period of 3 min into a suspension of fluorene (30 g, 182 mmol) and iron powder

Table 3. Some characteristics of polymers **VIIIa–VIIIc**

Polymer	η_{red}, dL/g (DMF, 25°C)	$\overline{M}_n \times 10^3$	$\overline{M}_w \times 10^3$	$\overline{M}_w/\overline{M}_n$	$T_{\text{ст}}$ (25°C)	$T_{10\%}$ (25°C)	
						air	argon
VIIIa	0.41	11.30	39.40	3.49	174	375	400
VIIIb	0.35	5.70	30.00	5.26	234	360	420
VIIIc	0.39	10.50	51.50	4.69	253	350	410



Absorption and fluorescence spectra of polymers (*1*) **VIIIa**, (*2*) **VIIIb**, and (*3*) **VIIIc** in chloroform ($c = 12.5 \times 10^{-4}$ mol/L, excitation with λ 350 nm).

(0.160 g, 2.86 mmol) in 200 mL of chloroform preliminarily cooled to 0°C, while the temperature was not allowed to raise above 5°C. Then the mixture was allowed to warm up to room temperature, and the reaction was carried out for 2 h. The resulting precipitate was filtered off and recrystallized from chloroform. The yield of **I** with mp 161–163°C was 54.5 g (93.2%).

2,7-Dibromo-9,9-dioctylfluorene (II). 1-Bromooctane (37.2 g, 194 mmol) was added to a suspension of compound **I** (30.0 g, 92 mmol), benzotriethylammonium chloride (0.18 g, 0.78 mmol), and sodium hydroxide (30 mL, 50 wt %) in 400 mL of DMSO. The reaction mixture was vigorously stirred at room temperature for 3 h. Then, it was extracted with diethyl ether, and the extract was washed with a saturated sodium chloride and dried by anhydrous magnesium sulfate. The solvent was evaporated. The residue was recrystallized from heptane. The yield of white crystals of **II** (mp 52–54°C) was 46.0 g (91.2%).

2,7-Bis(phenylethynyl)-9,9-dioctylfluorene (III). Compound **II** (10.96 g, 20 mmol), phenylacetylene (4.10 g, 40 mmol), 160 mL of triethylamine, palladium catalyst (0.098 g, 0.13 mmol), triphenylphosphine (0.10 g, 0.42 mmol), and copper(I) iodide (0.088 g, 0.46 mmol) were placed in a three-neck flask equipped with a stirrer, a reflux condenser, and an argon inlet tube. The reaction mixture was refluxed for 120 h. The resulting precipitate was filtered off. The filtrate was evaporated. The residue was recrystallized from hexane. The yield of **III** as light yellow crystals (mp 82–84°C) was 10.1 g (85.2%).

2,7-Bis(phenylglyoxalyl)-9,9-dioctylfluorene (IV). Compound **III** (10.05 g, 17 mmol), potassium permanganate (11.56 g, 73.15 mmol), 14.17 mL of water, 5.3 mL of acetic acid, and 350 mL of acetone were placed in a three-neck flask (500 mL) equipped with a stirrer, a reflux condenser, and a thermometer. The mixture was refluxed for 2.5 h. The reaction is accompanied by the deposition of black MnO_2. When the reaction was complete, the precipitate was filtered off and washed two times with hot acetone. Then, the filtrate was removed on a rotary evaporator. The residue was washed with distilled water to neutral pH, dried, and crystallized from heptane. The yield of bright yellow crystals of **IV** (mp 91–93°C) was 10.76 g (96.8%).

2,7-Bis(2',4',5'-triphenylcyclopentadienon-3'-yl)-9,9-dioctylfluorene (V). Compound **IV** (9.79 g, 14.45 mmol), 1,3-diphenylacetone (6.29 g, 29.9 mmol), and 400 mL of ethyl alcohol were placed in a three-neck flask (500 mL) equipped with a stirrer, a reflux condenser, and a dropping funnel. The reaction mixture was heated to gentle boiling, a solution of potassium hydroxide (0.85 g in 11.5 mL of water) was added, and the mixture was stirred for 2 h. The reaction mass was cooled. The resulting black precipitate was filtered off, washed with distilled water and cold alcohol, and crystallized from heptane. The yield of black crystals of **V** (mp 168–170°C) was 13.81 g (95.4%).

2,7-Bis(trimethylsilylethynyl)-9,9-dioctylfluorene (VI). Compound **I** (12.38 g, 38.24 mmol), trimethylsilylacetylene (9.36 g, 95.40 mmol), 500 mL of triethylamine, palladium catalyst (0.8 g, 1.08 mmol), triphenylphosphine (0.40, 1.53 mmol), and copper(I) iodide (0.22 g, 1.16 mmol) were placed in a three-neck flask (1 L) equipped with a stirrer, a reflux condenser, and an argon inlet tube. The reaction mixture was refluxed for 12 h. Then, the resulting precipitate was filtered off. The filtrate was evaporated on a rotary evaporator. The precipitate was crystallized from hexane. The yield of light yellow crystals of **VI** (mp 89–91°C) was 20.97 g (94.05%).

2,7-Bis(ethynyl)-9,9-dioctylfluorene (VII). A portion of 245 mL of methanol and 22 mL of a 20% aqueous potassium hydroxide were added to a vigorously stirred solution of compound **VI** (13.81 g, 23.69 mmol) in 440 mL of THF. The reaction mixture was stirred at room temperature for 10 h. The solvent was removed, and the residue was crystallized from hexane. The yield of white crystals of **VII** (mp 44–46°C) was 8.54 g (82.2%).

Synthesis of Polymers

Polymer VIIIa. Bis(cyclopentadienone) **V** (1.0034 g, 1 mmol) and bis(ethynyl) **VIIa** (0.4387 g, 1 mmol) were placed into a high-pressure stainless steel reactor (with an inner volume of 22 mL) preliminarily purged with carbon dioxide. A piston pump (High pressure equipment) was used for supplying liquid carbon dioxide and creating a required pressure of 200 bar at room temperature. The reactor was placed into a thermostat and slowly heated to 180°C, and the mixture was stirred for 10 h.

Then, after the reaction was complete, the reactor was cooled to room temperature, and stirring was switched off. The pressure was reduced to atmospheric, and the resulting polymer was dissolved in chloroform and salted out two times with methanol. The polymer was filtered off, washed with methanol, and dried in a vacuum drying cabinet for 24 h at 80°C.

^{1}H NMR ($CDCl_3$), δ, ppm: 6.81–7.61 (m, 44H, arom.), 0.85–3.52 (m, 68H, aliph.).

All PSPFs were synthesized analogously. Some characteristics of them are presented in Table 3.

Polymer VIIIb. ^{1}H NMR ($CDCl_3$, δ, ppm: 6.90–7.51 (m, 42H, arom.), 0.11–1.25 (m, 34H, aliph.).

Polymer VIIIc. ^{1}H NMR ($CDCl_3$, δ, ppm: 6.65–7.54 (m, 48H, arom.), 0.10–1.52 (m, 34H, aliph.).

ACKNOWLEDGMENTS

This work was supported by the International Science and Technology Center (project no. 3718), the Russian Academy of Sciences (under the aegis of the program "Design of New Metallic, Ceramic, Glass, Polymeric, and Composite Materials" of the Division of Chemistry and Materials Science, RAS), and the Presidium of the RAS (program no. P21 "Foundations of Basic Research of Nanotechnologies and Nanomaterials").

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