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POLYCONDENSATION

One-Pot Method for the Synthesis of Sulfonated Poly(1,3,4-oxadiazoles) Based on 4,4'-Oxydibenzoic Acid

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Abstract—A series of new copolymers of poly(1,3,4-oxadiazole) that contain side protogenic sulfo groups are synthesized by the direct copolycondensation of terephthalic and 4,4'-oxydibenzoic acids and hydrazine sulfate in oleum. Variation in the polycondensation conditions makes it possible to synthesize copolymers containing phenylene moieties with either 4-sulfo-10,10-dioxophenoxatiine or 4,4'-oxybis(3-sulfophenyl) moieties or a combination of the three moieties. This approach permits easy control over the physicochemical properties of the copolymers and the amount of protogenic sulfo groups. It is shown that the introduction of sulfonated moieties into copolymer molecules makes it possible to obtain materials with high values of ion-exchange capacity (1.5 mmol/g) and water absorption (110%), while the strength and thermal stability inherent in poly(*p*-phenylene 1,3,4-oxadiazoles) remain intact.

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A rapidly developing area of ecological energetics based on solid-polymer fuel cells has encouraged intensification of the allied lines of research aimed at production of cheap and reliable polymeric proton-conducting membranes. In this respect, of greatest interest are polymer electrolytes, in which protogenic groups are covalently linked to polymer macromolecules. Such materials are usually obtained either via the appropriate treatment (sulfonation or phosphorylation) of prefabricated macromolecular compounds or via the polymerization of monomers containing sulfo and phosphonic groups [1–4]. Since the 2000s, there has been an active search for an alternative to the expensive fluorinated proton-conducting membranes Nafion© (DuPont). The most promising polymeric electrolytes are the sulfonated aromatic condensation polymers poly(arylene ether sulfones) [5, 6], poly(arylene ether ketones) [7–9], and polyimides [10, 11], which are cheaper than the perfluorinated ones, feature high water absorption in a wide temperature range, and possess high thermal stability. Among polycondensation polymers are poly(1,3,4-oxadiazoles) (PODs) exhibiting excellent chemical resistance and thermal stability and having high glass-transition temperatures [12–16]. As a rule, POD polymers are modified by the introduction of side protogenic sulfo [17, 18] or phosphonic [19] groups via the polycondensation of hard-to-reach sulfonated or phosphorylated aromatic dicarboxylic acids or hydrazides. Recently, a number of studies devoted to the synthesis of sulfonated poly(arylene ether 1,3,4-oxadiazoles) have been published [20–23]. As a monomer, active 4,4'-oxydibenzoic acid was used; under the conditions of polycondensation with hydrazine sulfate in polyphosphoric acid at a high temperature, it yielded the partially sulfonated copolymers poly(arylene ether 1,3,4-oxadiazole) and poly(arylene ether 1,3,4-oxadiazole-1,2,4-triazole) [24–28]. The main drawback of this method is that the degrees of sulfonation of the resulting polymers cannot be controlled.

As was shown in [29], labile monomers (e.g., biphenyl-4,4'-dicarboxylic acid) can be used for the synthesis of thermally stable and fire-resistant sulfur-containing copolymers of poly(*p*-phenylene 1,3,4-oxadiazole) in the medium of oleum. Detailed research into the interaction of 4,4'-oxydibenzoic acid with strong sulfur-containing electrophiles [30] made it possible to develop a method for its use in the one-pot synthesis of a series of new sulfonated POD copolymers in oleum.

EXPERIMENTAL

Melting temperatures were measured on a Kofler bench equipped with a Hanna HI 93530 electron thermometer. NMR spectra were recorded on a Bruker Biospin Avance 500 spectrometer (operating frequencies of 500 and 125 for ^{1}H and ^{13}C spectra, respectively) in DMSO-d_6 or a D_2SO_4 solution. IR spectra were taken in the transmission mode on a Bruker Tensor 27 FTIR spectrometer (films or powders in KBr pellets as samples) in the range 4000–400 cm^{-1}. Thin films of POD copolymers were studied via placement of samples in the main beam of the spectrometer with an accumulation number of 32 and a sensitivity of 4 cm^{-1}. Elemental analysis was performed on a varioMICROcube elemental analyzer. The strengths and breaking energies of polymer films were measured with the aid of a Testometric M250-2.5CT test machine (Testometric Company Ltd.). The intrinsic viscosities of copolymer solutions were measured on an Ubbelohde viscometer with a capillary diameter of 0.99 mm at 25°C (concentrated sulfuric acid as a solvent). The oxygen indexes of copolymer films were determined on an Oxygen Index ASTM D 2863, BS ISO 4589-2 (Fire Testing Technology Ltd., United Kingdom) at a temperature of 21–22°C, an atmospheric pressure of 99.2–99.9 kPa, and a relative humidity of 62–64%; homogeneous film samples were used in measurements. The thermogravimetric analysis of the films was conducted on an STA 409 PC Luxx derivatograph (NETZCH, Germany) in air; the heating rate was 10 K/min.

The copolymers were synthesized with the use of the following compounds: terephthalic acid (TPA; CFR, China), reagent-grade hydrazine sulfate (HS; 98.5% of the main compound; Mosinter, China), 4,4'-oxydibenzoic acid (ODBA; Chemicalpoint, Germany), and reagent-grade oleum (20%, Yugreaktiv (GOST 2184-77)). Chlorosulfonic monomers were obtained with the use of chlorosulfonic acid (Sigma-Aldrich, Germany).

4,4'-Oxybis[3-(chlorosulfonyl)benzoic] Acid and 10,10-Dioxo-4-(chlorosulfonyl)-10λ^6-phenoxatiine-2,8-dicarboxylic Acid

Chlorosulfonic monomers were obtained by the interaction of ODBA and chlorosulfonic acid, as described in [29]. Prior to polycondensation, the initial reagents were dried in a desiccator over calcium chloride.

4,4′-Oxybis([3-(chlorosulfonyl)benzoic acid]) (2). The melting temperature was 230–231°C. IR (KBr): ν 1703 (CO); 1593 (C–C (Ar)); 1490 (C–C (Ar)); 1400, 1372 (SO_2Cl); 1261 (Ar–O–Ar); 1181 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6) δ (J, Hz): 6.94 (2H, d, $J = 8.5$, H-6,6′), 7.83 (2H, d. d, $J_1 = 8.5$, $J_2 = 2.5$, H-5,5′), 8.39 (2H, d, $J = 2.5$ H-3,3′) ppm.

10,10-Dioxo-4-(chlorosulfonyl)-10λ^6-phenoxatiine-2,8-dicarboxylic acid (3). The melting temperature was 268–269°C. IR (KBr): ν 1722 (CO), 1592 (C–C (Ar)), 1375 (SO_2Cl), 1327 (SO_2), 1216 (Ar–O–Ar), 1165 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6) δ (J, Hz): 8.37 (1H, d. d, $J_1 = 9$, $J_2 = 2$, H-7), 8.44 (1H; d; $J = 2$; H-1, H-3, or H-9), 8.48 (1H; d; $J = 2$; H-1, H-3, or H-9), 8.64 (1H; d; $J = 2$; H-1, H-3, or H-9) ppm.

Synthesis of Copolymers

The copolycondensation of dicarboxylic aromatic acids with a 20–100% excess of hydrazine sulfate was performed in oleum at 120°C. Solid components (hydrazine sulfate, aromatic dicarboxylic acids) were thoroughly mixed and dissolved in oleum (50 mL) at a temperature not above 50°C. The monomer ratio was calculated so that the polymer concentration in the resulting solution was 5–6%. The reaction was completed at the same viscosities of the reaction solution that were monitored from a change in the load on the stirrer axle; as a result, POD copolymers with close intrinsic viscosities were synthesized. The reaction was stopped by simultaneous cooling and dilution with concentrated sulfuric acid (96%); its amount was taken so that water occurring in sulfuric acid quenched the excess SO_3. It should be emphasized that the reactivities of the monomers are appreciably different. In the synthesis of copolymers containing 4-sulfo-10,10-dioxophenoxatiine (SDOP) moieties, times 20- to 30-fold longer than that in the case of the TPA-based homopolymer, as well as a large excess of HS (up to 100%), were needed to attain the desired values of viscosity. The rate of formation of the copolymers containing 4,4'-oxybis(3-sulfophenyl) (OBSP) moieties is comparable with the rate of polycondensation of TPA performed in a 50% excess of HS.

Method A. POD copolymers were synthesized with the use of the chlorosulfonyl derivative of phenoxatiine 3 (Method A1; Scheme (1)) or disulfochloride 2 (Method A2; Scheme (3)) and TPA at various ratios in the monomer mixture. Hydrogen chloride evolving during the synthesis via Method A has no effect on the reaction.

Method B. In the case of synthesis of POD copolymers containing SDOP moieties (Scheme (1)), the initially calculated amount of ODBA (1) was heated in oleum (50 mL) at a temperature of 120°C for 2 h. Under these conditions, a solution of 10,10-dioxo-4-(sulfo)-10λ^6-phenoxatiine-2,8-dicarboxylic acid (4) [30] in oleum was formed; it was then cooled to 50°C, calculated amounts of TPA and hydrazine sulfate were added (Method B1, Scheme (1)), and polycondensation was conducted via the above-described technique.

When POD copolymers containing OBSP moieties in polymer chains were prepared, the solid components ODBA, TPA, and HS were dissolved in oleum (50 mL) and polycondensation was conducted via the standard technique (Method B2; Scheme (3)).

Method C. For three-component POD copolymers containing *p*-phenylene, SDOP, and OBSP moieties in macromolecular chains, polycondensation was conducted in a stepwise manner (Scheme (4)). At the first step, the solution of aromatic sulfonic acid 4 in oleum was obtained from the calculated amount of ODBA via Method B1 (scheme (1)); the reaction mixture was cooled to 50°C; the required amounts of ODBA, TPA, and HS were added; and polycondensation was performed as described in Method B2 (Scheme (3)). In addition, these POD copolymers may be synthesized via the copolycondensation of sulfo chlorides 2 and 3 with TPA and HS in oleum at 120°C.

The films were formed via pouring of an even layer of a 3% polymer solution in sulfuric acid on a glass substrate. To avoid the formation of defects, the polymer solution was preliminarily outgassed in vacuum or centrifuged. Subsequent coagulation was performed in a 70–72% sulfuric acid solution. Under these conditions coagulation occurred slowly; as a consequence, films without any visible defects were obtained. The films were detached from the glass substrate and rinsed successively for 10 min with running water, for 20 min with a 10% aqueous solution of sodium bicarbonate, and again with water. This procedure provided almost full removal of sulfuric acid residues from the film depth, as confirmed by the data of elemental analysis. The wet film was pulled on a plastic frame and allowed to stay for 48 h at room temperature. The mechanical characteristics were determined with the use of polymer films with dimensions of 50 mm × 10 mm × (0.04–0.075) mm. For each sample of the POD copolymer, 15 measurements were made with an error of 5–8%.

The amount of water absorbed by a polymer film was estimated via measurements of the difference in masses of the dry and wet film. The mass of the dry sample, m_{dry}, was determined via weighing of a film dried to a constant mass in vacuum at a temperature of 120°C in a drying box. The resulting sample was placed in distilled water for 24 h at room temperature. The excess water was removed from the surface of the polymer film via squeezing of it between sheets of filter paper, and the mass of the wet sample, m_{wet}, was determined via weighing. The absorption of water (wt %) was calculated through the formula

$$\text{Water absorption} = \frac{m_{\text{wet}} - m_{\text{dry}}}{m_{\text{dry}}} \times 100\%$$

$$\text{and} \quad [H_2O/-SO_3H] = \frac{n(H_2O)}{p(-SO_3H)},$$

where $[H_2O/-SO_3H]$ is the number of moles of H_2O per mole of SO_3H groups in a polymer, $n(H_2O)$ is the number of moles of absorbed water in the wet sample, and $p(-SO_3H)$ is the number of moles of sulfo groups in the sample.

Ion-exchange capacity (IEC) was determined via direct titration in the presence of phenolphthalein as an indicator. In order to obtained the acidic form, film samples were sequentially placed in a 0.01 H HCl solution for 12 h at room temperature, rinsed with distilled water, and soaked in a 2.5 mol/L NaCl aqueous solution for 24 h at room temperature. The films were taken off and rinsed with distilled water (3 × 15 mL). Aqueous solutions were combined and titrated with 0.01 H NaOH (C_{NaOH}). The ion-exchange capacity (mmol/g) was calculated through the formula

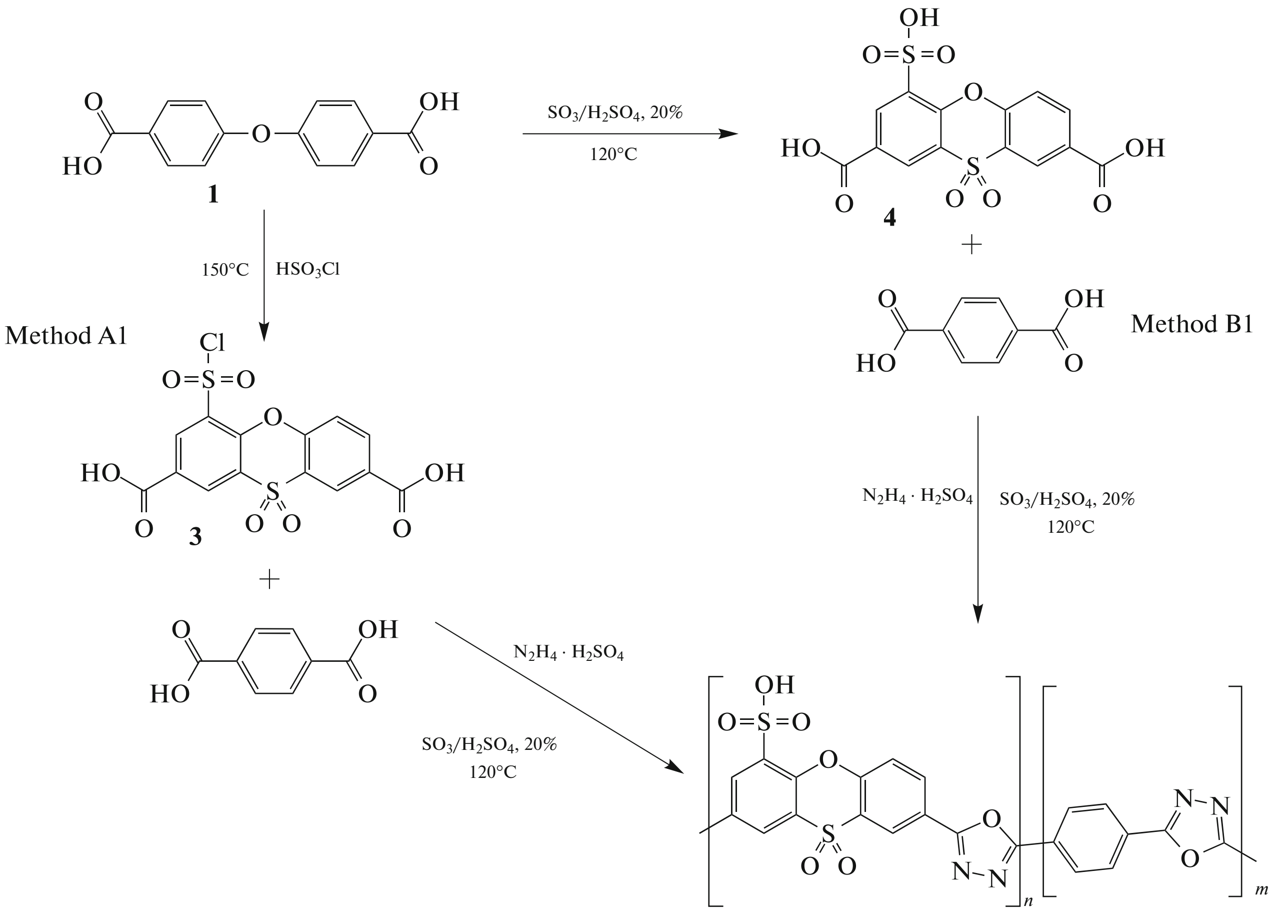
$$\text{IEC} = \frac{C_{\text{NaOH}} V_{\text{NaOH}}}{m_{\text{dry}}},$$

where V_{NaOH} is the volume of 0.01 H NaOH consumed in the titration.

RESULTS AND DISCUSSION

The method developed for the one-pot synthesis of sulfonated poly(arylene 1,3,4-oxadiazoles) allows, making use the features of interaction between 4,4'-oxydibenzoic acid and oleum, to obtain copolymers containing SDOP or OBSP moieties or their combination in macromolecular chains in well-controlled proportions in the one-step. Three sets of such copolymers containing various amounts of protogenic moieties were synthesized, and their physicochemical and mechanical properties were studied. For the sake of comparison, the homopolymer based on TPA—POD-0 was used. Samples POD-1–POD-14 were irregular copolymers containing various (from 2.5 to 70.0) mass fractions of SDOP units. Series POD-7–POD-14 was synthesized by the polycondensation of ODBA, TPA, and hydrazine sulfate in oleum via Method B1 (Scheme (1)). The series of copolymers POD-1–POD-6 with similar compositions was obtained through the polycondensation of chlorosulfonyl derivative of phenoxatiine 3 via Method A1 (Scheme (1)). The compositions of the copolymers were identical, as evidenced by IR analysis, NMR spectroscopy, and elemental analysis.

The appearance of sulfur in the samples indicates that SDOP units are incorporated into polymer chains and that the corresponding copolymers are formed. The compositions were determined from the ratios of mass fractions of sulfur and carbon, which were derived from the elemental



Method A1: POD-1–POD-6
Method B1: POD-7–POD-14, POD-27

analysis of the samples. The finding that there is coincidence between the experimental and theoretical values is evidence that SDOP moieties are fully incorporated into macromolecules of the corresponding copolymer.

In the analysis of the IR spectra (Fig. 1a) obtained for the POD-1—POD-14 samples and the POD-0 homopolymer, the occurrence of the SDOP moieties in the copolymer macromolecules was reliably confirmed by the presence of two sets of absorption bands corresponding to asymmetric and symmetric stretching vibrations of various S=O groups. One set of bands occurs at 1310 and 1165 cm^{-1} and corresponds to the stretching vibrations of the cyclic group SO_2. The other set of bands at 1250, 1200, and 1040 cm^{-1} corresponds to analogous signals due to the sulfo-acid group occurring in the hydrated form. It is clear that the intensity of these bands depends on the content of SDOP units.

A comparison of the IR spectra of copolymers POD-7—POD-14 prepared via Methods B1 (Scheme (1)) and series POD-1—POD-6 showed that the positions and intensities of all the characteristic absorption bands coincide. This result confirms that Methods A1 and B1 are equivalent. The distinctive feature of preparing SDOP copolymers with high intrinsic viscosities consists in the necessity to use large excesses of HS and oleum. The reaction occurs much slower and is accompanied by strong gas evolution; this finding suggests that the side process occurs. The qualitative analysis of the gas mixture revealed the presence of nitrogen and sulfur dioxide. It is probable that the presence of aromatic sulfonic acid 4 leads to the partial formation of *N,N*-acylsulfonyl hydrazines. The latter may be transformed into *N,N*-diacylhydrazines, similarly to the McFadyen—Stevens reaction, which is known for aromatic acylhydrazides bearing electron-acceptor groups [31, 32]. Presumably, the side process may be presented by the following scheme, (2), a fact that explains deceleration of the polycondensation reaction and the necessity to use considerable additional amounts of HS and oleum.

The occurrence of this process is indirectly confirmed by the visual evolution of gas during the classical polycondensation of TPA and HS in the presence of *p*-toluenesulfonic acid.

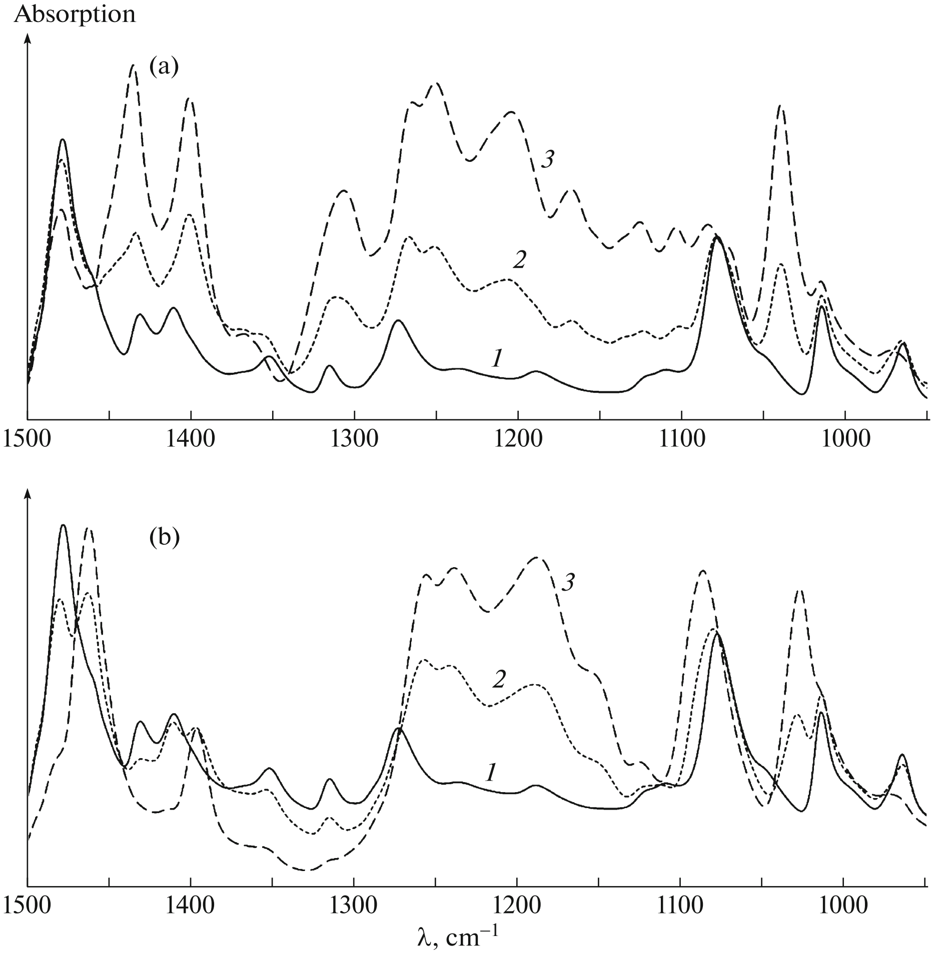
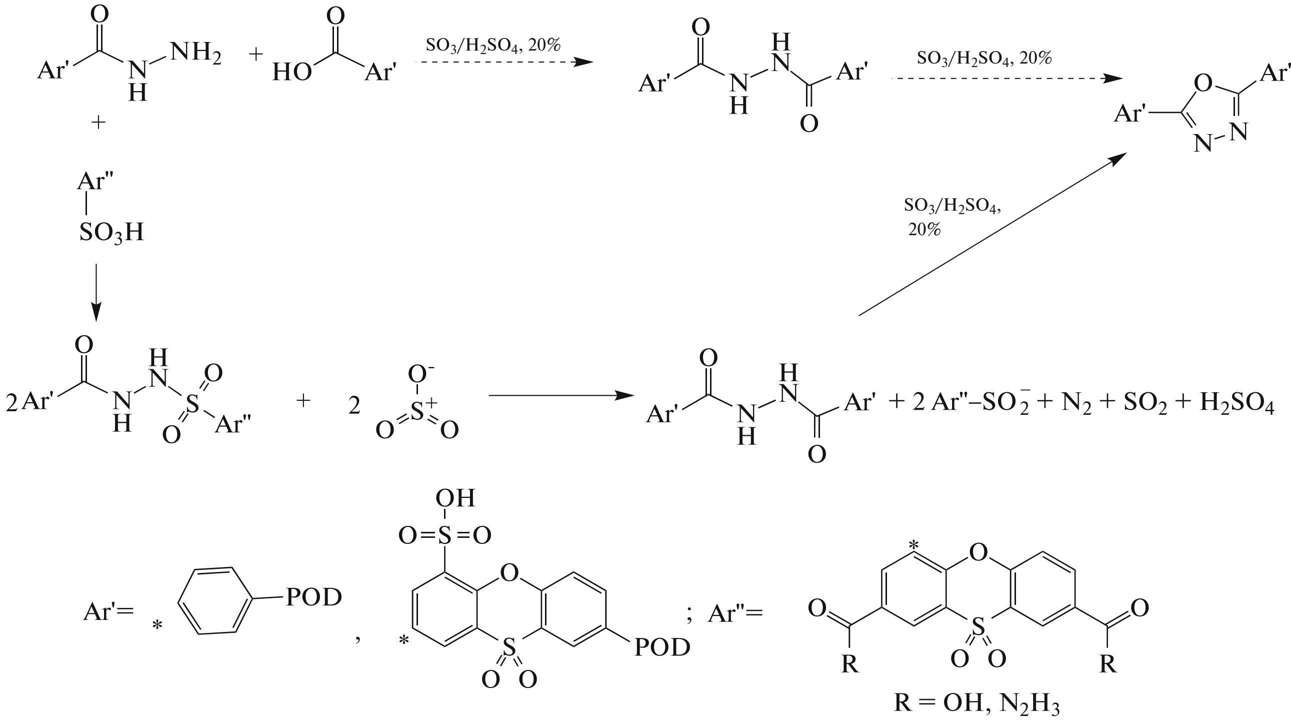
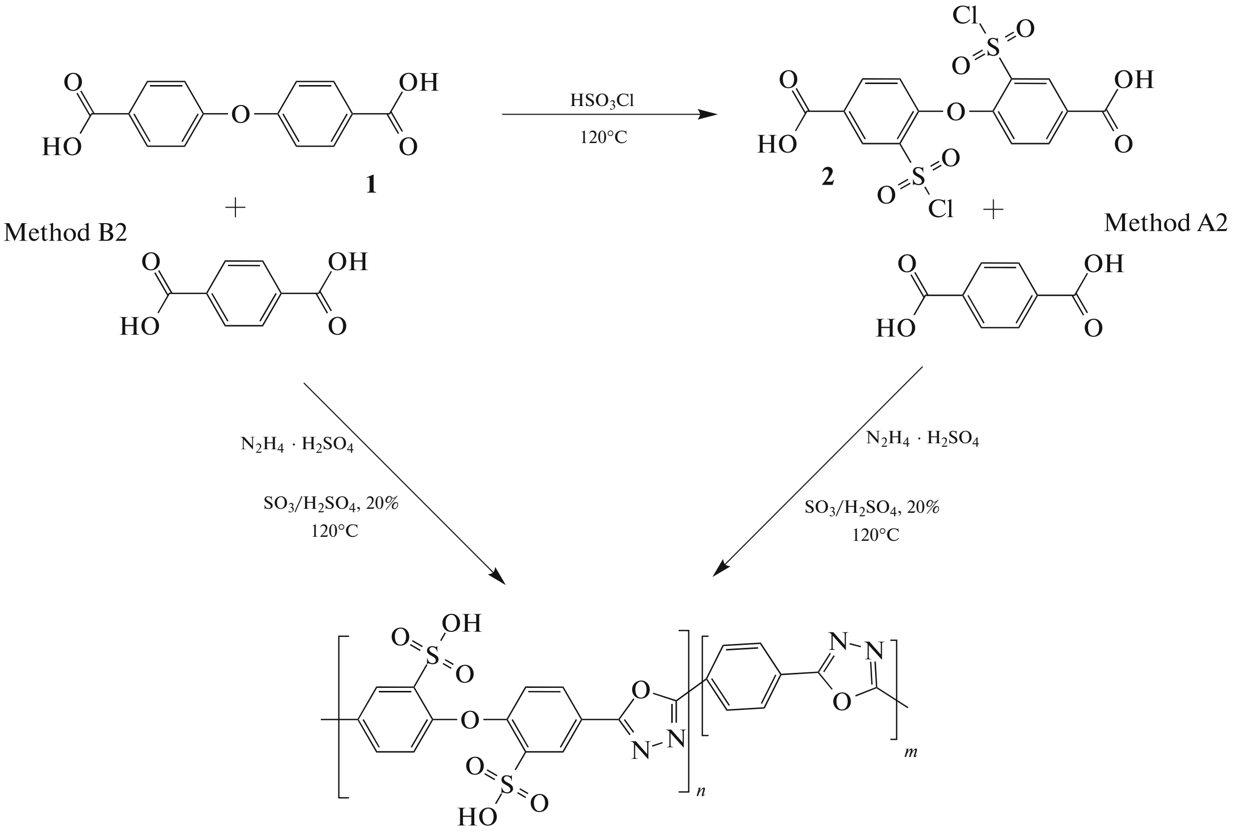


Fig. 1. IR spectra of (a) SDOP copolymers (*1*) POD-0, (*2*) POD-4, (*3*) POD-6 and (b) OBSP copolymers (*1*) POD-0, (*2*) POD-18, and (*3*) POD-22.



In the case of the polycondensation of TPA and ODBA with HS performed via Method B2, when the solution of ingredients in oleum was gradually heated to 120°C, the copolymers containing only OBSP moieties were formed (Scheme (3)). Probably, the formation of oligomeric and polymeric hydrazides and sulfonation in the ortho position of ODBA occur in parallel at temperatures lower those required for formation of the phenoxatiine ring.



Method B2: POD-15–POD-24

Hence, at the initial stage, polyhydrazide that already contains OBSP units is formed. A further increase in temperature leads to the formation of only the oxadiazole cycle, and no cyclization into SDOP moieties occurs, because of strong steric hindrances in a polymer macromolecule. This circumstance provides a high rate for the polycondensation of ODBA and TPA and very weak gas evolution because, here, unlike in the synthesis of SDOP copolymers, free arylsulfonic acid is practically absent from the reaction mixture. With the use of this method, nine irregular copolymers POD-15—POD-23 with mass fractions of OBSP units from 5 to 90 were synthesized. As in the previous case, the appearance of sulfur in samples POD-15—POD-23 suggests that OBSP moieties are incorporated into polymer macromolecules. The mass ratio of carbon and sulfur suggests the formation of the disulfo-derivative of ODBA in an amount corresponding to the composition of the initial monomer mixture. Thereby, the content of protogenic sulfo groups may be varied via the introduction of various amounts of ODBA units into the polycondensation reaction.

The fact that the copolymer of 4,4′-oxybis(3-sulfobenzoic) acid is formed is reliably confirmed by IR and ^{1}H NMR studies. As opposed to the IR spectra of copolymers POD-1—POD-14, the IR spectra of POD-15—POD-23 samples show only absorption bands at 1250, 1200, and 1040 cm^{-1}, corresponding to the asymmetric and symmetric stretching vibrations of various S=O sulfonic groups occurring in the hydrated from (Fig. 1b).

Marked differences are additionally observed in the ^{1}H NMR spectra of SDOP and OBSP copolymers and poly(*p*-phenylene 1,3,4-oxadiazole). For comparison, POD-6 and POD-22 copolymers, which have approximately equal molar ratios of SDOP and OBSP

Table 1. Some characteristics of POD copolymers

POD copolymer	Content of units, wt %	Breaking strength σ_b, MPa	Elastic modulus E, GPa	[η], dL/g (conc. H_2SO_4, 25°C)	Oxygen index, %
SDOP	2.5	33.1	3.3	1.60	23.2
	10	32.8	3.0	1.01	25.4
	20	32.3	1.7	1.19	26.6
	30	37.3	1.5	1.02	27.8
	50	36.5	1.3	1.17	29.8
	70	33.8	2.3	1.11	30.9
OBSP	5	48.8	4.1	1.99	23.7
	10	47.2	3.6	1.87	25.6
	20	39.5	2.6	1.98	25.7
	30	10.5	2.1	1.81	28.0
	50	6.5	1.6	1.62	28.8

For poly(*p*-phenylene 1,3,4-oxadiazole) (POD-0), $\sigma_b = 31.8$ MPa, $E = 3.2$ GPa, [η] = 1.60 dL/g, and the oxygen index is 22.8.

units and phenylene moieties, were chosen. The spectra were recorded in deuterated sulfuric acid, and a signal at 12.0 ppm, due to ^1H nuclei in D_2SO_4, was used as an internal standard. In the spectrum of homopolymer POD-0 (Fig. 2a), there is a signal at 9.67 ppm, which corresponds to four equivalent protons of the phenylene moiety in the form of a broadened singlet.

The spectrum of the POD-22 sample exhibits three sets of signals due to protons in phenylene and symmetric moieties of the OBSP copolymer. Protons occurring in the ortho position to sulfo groups appear as a two-proton doublet at 10.0 ppm. The broadened singlet at 8.68 ppm corresponds to the ortho position of the ether group, and the six-proton broadened singlet at 9.67 ppm corresponds to four protons of the phenylene moiety and two protons of OBSP units occurring in the para position with respect to sulfo groups in the aromatic ring (Fig. 2b).

In the case of the copolymer POD-6, the ^1H NMR spectrum has a more complex pattern; however, signals corresponding to all five protons of the SDOP moiety and four protons of the phenylene unit may be identified (Fig. 2c). For example, the signals of three protons of the SDOP moiety occurring in ortho positions with respect to electron-acceptor groups appear in a weaker field in the form of three multiplets at 10.42–10.35, 10.29–10.24, and 10.22–10.16 ppm. Broadened singlets at 9.78 and 9.13 ppm are attributed to the remaining two protons of the phenoxatiine heterocycle. Protons of the phenylene moiety are observed in the form of a broadened singlet at 9.67 ppm.

Some characteristics of the films based on SDOP and OBSP copolymers are listed in Table 1. In the case of copolymers POD-1–POD-6, an increase in the content of phenoxatiine moieties causes a more than twofold reduction in elastic modulus and entails improvement of strength characteristics relative to those of the TPA-based homopolymer. The best result is obtained for the films containing 50% SDOP moieties; however, the synthesis of this copolymer is very time-consuming.

In the case of copolymers POD-15–POD-23, the introduction of more than 30% OBSP moieties considerably worsens the physicochemical characteristics of the polymers. When more than 50% OBSP moieties were introduced, no films were obtained.

As is seen from the TGA and DTA curves shown in Fig. 3, for polymers POD-0, POD-6, POD-20, the introduction of SDOP or OBSP moieties has practically no effect on the thermal stability of the POD copolymers. The mass loss in the range 100–220°C corresponds to the removal of equilibrium water, whose amount is as high as 15–18%. The onset temperature of degradation of the copolymer samples is 460–475°C, and the maximum of mass loss is observed at a temperature of 500–510°C. At this temperature, the destruction of oxadiazole cycles via one of the least strong C–O–C bonds probably begins. At a higher temperature in the range 530–650°C, destruction of the carbon skeleton occurs and the mass

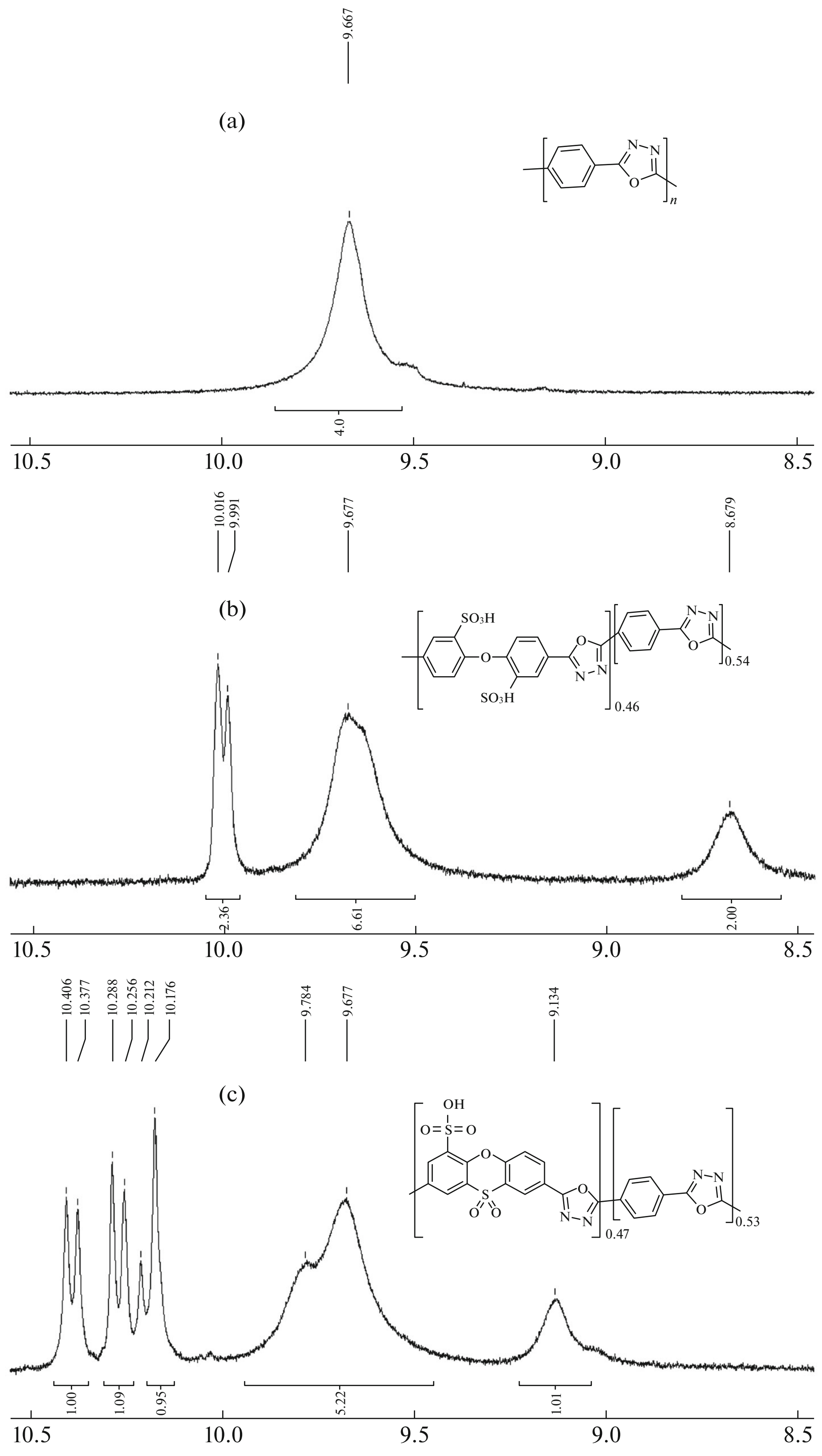


Fig. 2. ^{1}H NMR spectrum of (a) homopolymer POD-0 and (b, c) copolymers (b) POD-22 and (c) POD-6.

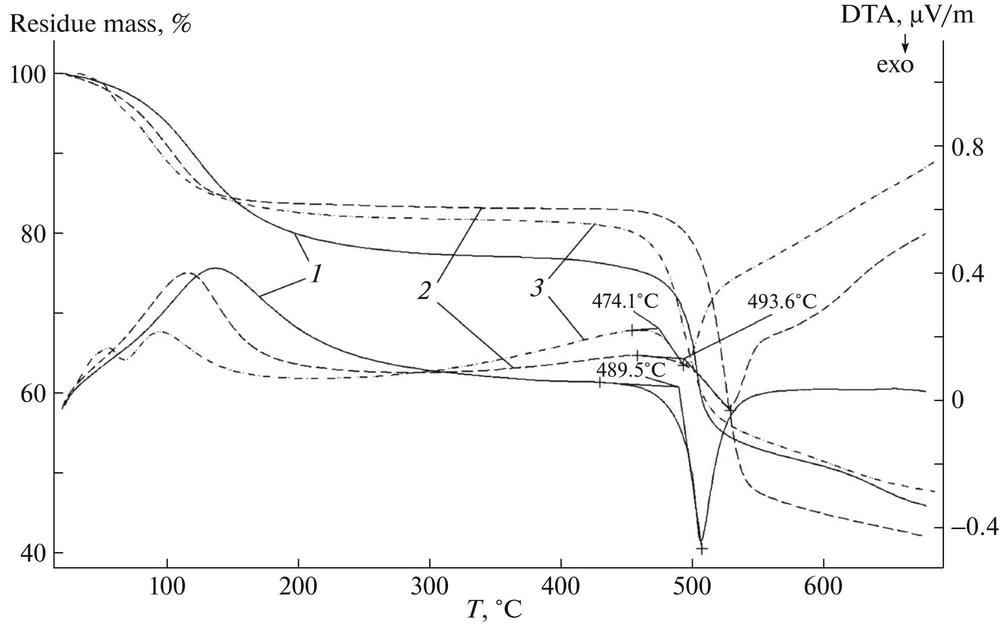


Fig. 3. TGA and DTA of polymers (*1*) POD-6, (*2*) POD-0, and (*3*) POD-20.

loss is about 50–60% of the total copolymer mass. Destruction occurs less intensely. Hence, it follows that the thermal stability of POD polymers is largely determined by the strength of the oxadiazole cycle in the polymer chain.

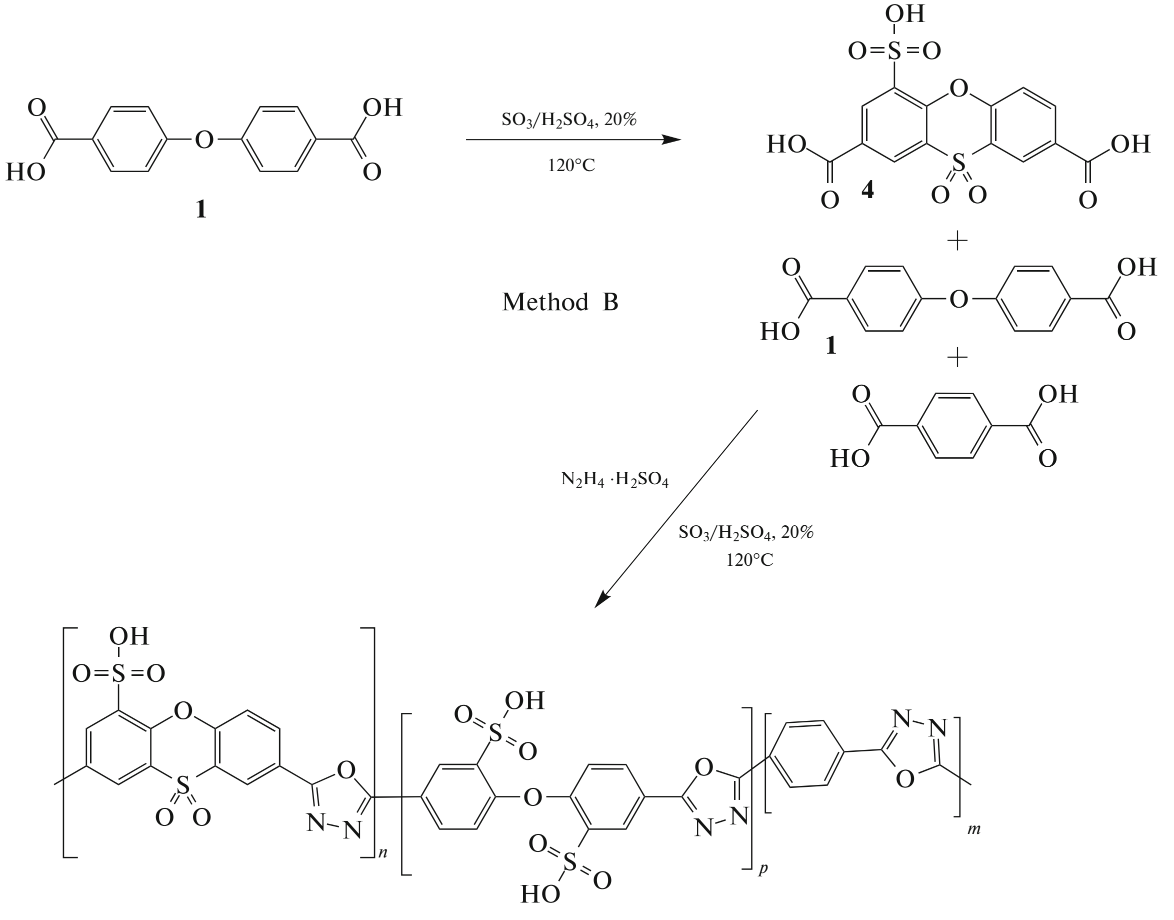
The fire resistance of all the POD copolymers (Table 1) monotonically increases with an increase in the amount of sulfo-containing units. The introduction of 50 wt % SDOP or OBSP makes it possible to increase the limiting oxygen index by 6–7%.

A comparison of ion-exchange capacities of copolymers showed that, as the contents of both SDOP and OBSP units in polymer chains increase, the IECs grow proportionally and may reach 2 mmol/g (Table 2, POD-6). This value is a factor of 2 greater than that for Nafion© films. However, the synthesis of the copolymers containing a large amount of SDOP moieties occurs very slowly and requires the use of large excesses of HS and oleum. As regards OBSP copolymers, the high IECs are achieved at such concentrations of OBSP moieties that the physicomechanical characteristics of the polymer preclude the formation of strong films.

On the basis of the above evidence, it was proposed that the introduction of both sulfonated moieties into copolymer macromolecules will make it possible to obtain a thermally stable material combining high physicomechanical and ion-exchange characteristics. For this purpose, a one-pot synthesis that allows the synthesis of a POD copolymer containing the desired amounts of SDOP and OBSP moieties via one stage (Method C, Scheme (4)) was developed.

Table 2. Ion-exchange characteristics of SDOP copolymers

Copolymer	Content of SDOP units, wt %	IEC, mmol/g		Content of water, wt %	Water absorption, wt %
		calcd.	found		
POD-2	10	0.27	0.22	19.1	72.3
POD-4	30	0.79	0.71	20.3	98.8
POD-5	50	1.32	1.21	21.8	107.5
POD-6	70	1.98	1.95	22.5	110.1



POD-25–POD-26

To investigate the properties of new polymers, the series of copolymers POD-24–POD-27 was synthesized; in it, equal (1.5 mmol/g) amounts of protogenic sulfo groups in macromolecules were attained with the use of various combinations of SDOP and OBSP moieties. Samples POD-25 and POD-26 were ternary copolymers with mass fractions of SDOP and OBSP moieties of 20 : 20 and 40 : 10, respectively. For comparison, binary copolymers containing either only *p*-phenylene and SDOP moieties (POD-27) or *p*-phenylene and OBSP moieties (POD-24) were prepared. All the samples except POD-27 had high intrinsic viscosities. In the case of copolymer POD-27, we failed to attain a high value of [η], even if the reaction was performed over 100 h. The physicochemical and mechanical characteristics of the films based on the studied copolymers are summarized in Table 3.

All the films showed high strength characteristics, and the samples containing SDOP moieties featured increased elasticity. The optimum balance between strength and elasticity was attained at an equimolar ratio of SDOP and OBSP moieties in macromolecular chains.

The ion-exchange capacity of the polymer materials is a factor characterizing the amount of ionizable protogenic groups responsible for proton conductivity. As is clear from the above experimental data, for all the samples, the accessibility of sulfo groups for exchange is above 90%. In the case of POD-25, it is practically equal to the theoretical value. In addition, the introduction of SDOP moieties into the polymers probably leads to the formation of a branched system of ionic channels that provides improved accessibility of protogenic groups. This assumption is indirectly confirmed by marked increases in water absorption and the equilibrium content of water in the films based on SDOP copolymers and, as was noted above, by growth in the IEC.

Thus, the one-pot method of synthesis of sulfonated poly(arylene-1,3,4-oxadiazoles), which makes it possible, with consideration for features of the interaction of 4,4'-oxydibenzoic acid with oleum, to synthesize in one stage POD copolymers containing in mac-

Table 3. Physicochemical and mechanical characteristics of POD-24—POD-27

Copolymer	SDOP, wt %	OBSP, wt %	Breaking strength, MPa	Relative elongation at break, %	Elastic modulus, GPa	[η], dL/g (conc. H_2SO_4, 25°C)	IEC,* mmol/g	Water content, wt %	Water absorption	
									wt %	$[H_2O/-SO_3H]$
POD-24	0	30	58.8	2.8	2.1	2.3	1.39	18.2	78.6	29.1
POD-25	20	20	55.1	9.0	0.6	2.5	1.49	19.8	112.4	41.6
POD-26	40	10	53.1	5.6	0.9	2.2	1.37	21.1	108.0	40.0
POD-27	60	0	32.1	1.5	0.2	1.0	1.38	22.0	111.5	41.3

*Calculated, 1.5 mmol/g.

romolecular chain *p*-phenylene moieties with either 4-sulfo-10,10-dioxophenoxatiine moieties or 4,4'-oxybis(3-sulfophenyl) moieties or their triple combination at well-controlled ratios was elaborated. The introduction of sulfonated moieties into copolymer macromolecules provides a way to obtain materials possessing high values of the IEC (1.5 mmol/g) and water absorption (110%) and preserving the strength and thermal stability inherent in poly(*p*-phenylene 1,3,4-oxadiazoles). The obtained copolymers and the films formed on their basis may be of interest as proton-conducting membranes for solid-polymer fuel cells.

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