Poly(arylene oxides) (PAOs) [1–3] constitute a vast class of aromatic condensation polymers, including poly(phenylene oxides) (PPOs) [1–3], poly(ether sulfones) (PESs) [1–5], poly(ether ketones) (PEKs) [1–3, 5–8], etc. PAOs are prepared through various reactions of polymer synthesis [1–3]; however, the synthesis of PAOs via nucleophilic aromatic displacement reactions has enjoyed the widest application [9, 10]. In most cases, these reactions are based on the polycondensation of alkali-metal bisphenolates with activated electrophilic monomers, arylenedinitro compounds [11–13] and arylenedihalide compounds [14, 15].

PAOs and especially PESs and PEKs are characterized by high heat resistance and chemical resistance and excellent thermal stability; this circumstance has motivated the manufacture of high-performance thermoplastics based on these polymers [16–19]. Owing to the above-mentioned features, PAOs show promise as base polymers for production of proton-exchange membranes applicable for fuel cells, which have attracted considerable attention as ecologically friendly and effective energy systems [20–35]. Severe exploitation conditions of fuel cells (elevated temperatures, the high activity of water, and the appearance of highly reactive oxidizing radicals) require that proton-exchange membranes should possess high hydrolytic resistance and thermo-oxidative and electrochemical stability.

To impart proton conductivity to PAOs, protogenic groups, among which sulfo acid moieties are most widely used, are usually incorporated into their macromolecules. Over the past two decades, a considerable step forward has been made in this field. Analysis of these achievements is the goal of this review.

**SYNTHESIS OF PAOS CONTAINING PROTOGENIC GROUPS**

The overwhelming majority of PAOs containing protogenic (sulfo acid) groups are prepared with the use of the following common methods: via sulfonation of the preformed PAOs [23–33, 35]; through nucleophilic aromatic displacement reactions with participation of sulfonated monomers [23–33, 35]; and derivatization of PAOs with reactive groups under the action of reagents containing protogenic groups in the explicit or latent form [34].

**SYNTHESIS OF PAOS CONTAINING PROTOGENIC GROUPS THROUGH SULFONATION OF PREFORMED PAOS**

The simplest method of preparing PAOs containing protogenic groups includes the sulfonation of preformed high-molecular-mass PAOs [23–33].
Sulfonation is an electrophilic displacement reaction [36, 37], which significantly depends on the nature of substituents in cycles of PAO macromolecules. Namely, electron-donor substituents facilitate the reaction, whereas electron-acceptor substituents hamper it.

The sulfonation of PAOs is implemented with the use of well-known sulfonating agents: sulfuric acid [38], chlorosulfonic acid [39], pure SO₃ or SO₃-based mixtures [40–43], and acetyl sulfate [44].

In the case of fuming H₂SO₄ or chlorosulfonic acid, sulfonation is sometimes accompanied by the degradation of PAOs [45]. The rate of sulfonation of PAOs in H₂SO₄ can be governed through variation of the time of reaction and the concentration of acid [44]. Thus, targeted PAOs with a degree of sulfonation of 30–100% can be synthesized without any chemical degradation or crosslinking of the polymer [46].

Among sulfonated PAOs, various poly(p-phenylene oxides) [41, 47–50] and especially PEKs, such as poly(ether ether ketones) (PEEKs) [38, 42, 51–55] and PESs [54, 56–65], have attracted considerable attention from researchers.

It is quite natural that the first sulfonated PAOs were synthesized from polymers produced on a commercial or pilot scale: poly[2,6-dimethyl(phenylene oxide)] [41, 47–49], PEEKs [38, 53–55], and Udel poly(ether sulfone) [40, 56–61].

The sulfonation reactions of these polymers with the most frequently used sulfonating agents (chlorosulfonic acid and concentrated sulfonic acid) proceed in accordance with the following schemes.