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# Dimethyl sulfoxide as a green solvent for successful precipitative polyheterocyclization based on nucleophilic aromatic substitution, resulting in high molecular weight PIM-1

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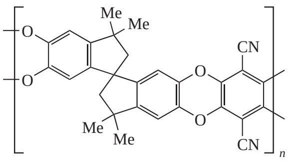
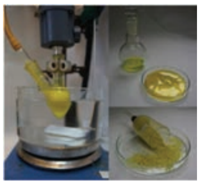
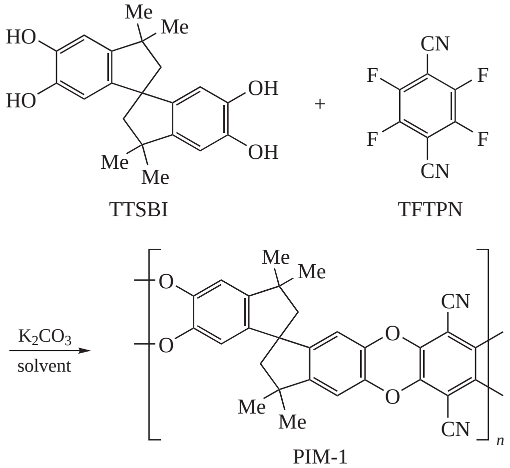
**A new method for the effective synthesis of high molecular weight polymer of intrinsic microporosity (PIM-1) powder widely employed for gas separation membranes was successfully developed using precipitative polyheterocyclization process in non-toxic DMSO.**





Many highly porous polymers are of interest due to their unique features.[1–3] Polymers of intrinsic microporosity (PIMs) synthesized over the last decade attract considerable attention owing to their outstanding and unusual gas separation properties.[1,3] The most investigated PIM is a so-called PIM-1, partially ladder spiroindanobenzodioxane polymer based on commercially available 5,5′,6,6′-tetrahydroxy-3,3,3′,3′-tetramethylspirobisindane (TTSBI) and 2,3,5,6-tetrafluoroterephthalonitrile (TFTPN).



**Scheme 1**

It was prepared by aromatic nucleophilic polyheterocyclocondensation (Scheme 1) *via* three mostly used procedures: reaction in DMF[1] at 65 °C for 24–96 h, fast synthesis[4] in DMA/toluene (or diethylbenzene) at 155 °C for ~10 min or polycyclocondensation in NMP[5] at 60 °C for 24 h. The prepared so far PIM-1 polymers of high molecular weight ($M_w$), up to 270 kDa relative polystyrene (PS) standards, were characterized by a large variety of polydispersity index (PDI) values (from 2 to 15). The presence of significant amount of macrocyclic oligomers in polycondensation products obtained at low temperatures and low initial monomer concentrations ($\leqslant$ 10 wt%) was proved in many studies.[1,3–5] It was shown[4] that additional purification from cyclic oligomers or gel fraction is always required for the preparation of PIM-1 based films (gas separation membranes) of reasonable quality. During this process, the loss of highly cost polymer reaches 10–30% of the synthesized one. The films produced from THF solutions of PIM-1 synthesized as described[1] without further fractional purification (PDI ~8.7) were found to be so brittle that it makes their strength and gas permeability measurements impossible. The purified polymers or the ones obtained in the fast synthesis in DMA/toluene (diethylbenzene) at 155 °C for ~10 min[4] with lower PDI (1.7–2.5) allow one to prepare self-supporting films with a tensile stress at break and an elongation at break reaching 49.7 MPa and 15.8%, respectively.[4] The aforementioned strength properties for the PIM-1 based film definitely do not meet the requirements for many applications (*e.g.*, for PIM-1 hollow fiber membrane production). So that, a search for new effective methods of PIM-1 synthesis is still of current interest. Evidently, the process performance should be improved by decreasing energy consumption and simplification of the polymer isolation and purification. For environmental requirements, the rejection of toxic polar aprotic solvent (DMF, DMA, NMP, *etc*.) usage and search for their replacement is encouraged.[6] The need to replace polar aprotic solvents is caused by their designation as reproductive toxins and the related legislation that is coming into force. Also, the mixed organic-aqueous waste which results from the processes with these solvents is difficult to purify or incinerate. The evident alternative to these solvents is DMSO being a non-toxic high-boiling polar aprotic solvent which was not used for PIM-1 synthesis, probably, because the polymer is almost insoluble in it. From our point of view, it does not make a high $M_w$ polymer synthesis impossible. Earlier we studied a precipitative polyheterocyclocondensation of aromatic tetracarboxylic acid dianhydrides with aromatic di- and tetraamines in phenols.[7,8] The reaction led to polynaphthoyleneimidobenzimidazole (PNIB)[7] and polynaphthoylenebenzimidazole (PNBI),[8] which are insoluble in phenols. During the polycondensation process, high $M_w$ polymer precipitates in a form of a fine dispersed powder which can be separated from the solvent by simple filtration without usage of precipitator. Also, the separated solvent may be reused without additional distillation. After acetone or ethanol extraction (to remove the remains of phenol solvent) the polymer powder can be used for fiber and moulded material production.

Exceptional gas separation properties of PIM-1 and the necessity of broad investigations for membranes based on it were reported.[1,3–5] Therefore, modern and environmentally friendly technology is required for PIM-1 production. Current methods of heterocyclic high-performance polymer synthesis and processing require toxic amide solvents, and DMSO would be an excellent alternative.

In this work, we have successfully applied our experience to aromatic nucleophilic polyheterocyclocondensation of TTSBI and TFTPN (see Scheme 1). The reaction occurs as a precipitative process in DMSO media in the presence of $K_2CO_3$ at 60–120 °C for 2–7 h. As a result, the PIM-1 forms as a polymeric fine dispersed high $M_w$ powder in almost quantitative yield. The data on the polymer synthesis and properties are given in Table S1 (see Online Supplementary Materials). The chemical structure of the polymer powder form was identical to that obtained by the other known methods[1,3–5] as shown by FTIR, $^1$H and $^{13}$C NMR (Figures S1–S3). Mechanical properties of films cast from $CHCl_3$ on glass plates based on these samples were also tested. Sample 4 (Table S1) obtained by the Budd method[1] gave a film with a tensile stress at break of 32.7 MPa and an elongation at break of 5.8%. Sample 3 synthesized by the new method makes it possible to improve film tensile strength properties up to 55.6 MPa and 22%, respectively. The molecular weight distribution (MWD) characteristics for the obtained by the new method PIM-1 were studied more precisely because they sufficiently affect the film tensile strength properties. It is well understood that the total MWD on polycondensation reflects a sum of those of linear chains and cyclic oligomers. Therefore, the higher the extent of reaction (and consequently the molecular weights of linear part), the higher the polydispersity index (PDI) of total reaction product.[9,10] In particular, it was shown in numerous studies that the nucleophilic aromatic substitution polycondensation is accompanied by cyclization reactions. The detailed analysis of cyclic oligomer amounts in poly(arylene ether ketone)s based on bisphenol A has been performed. The determined cyclization constants were found to be well consistent with the values calculated in accordance with the Jacobson–Stockmayer theory for thermodynamically controlled cyclization process.[11] In principle, due to the structural features of monomers, leading to PIM-1 polycondensation processes make possible not only cyclization reactions but, also, branching and cross-linking.[4,12] Moreover, it can be reflected in molecular inhomogeneity of products including their MWD. MWD curves for the samples synthesized at different temperatures are shown in Figure 1.

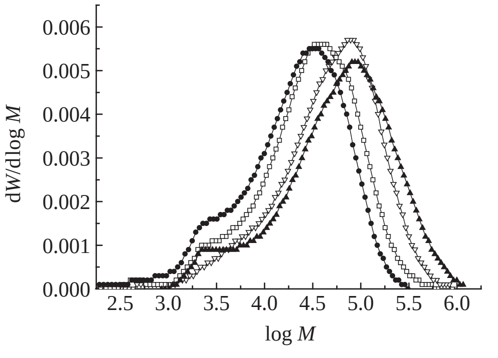


**Figure 1** MWD curves (relative PS) of PIM-1 prepared in DMSO at various temperatures: (●) 60, (□) 100 and (▲) 120 °C and (▽) in DMF by described[1] method.

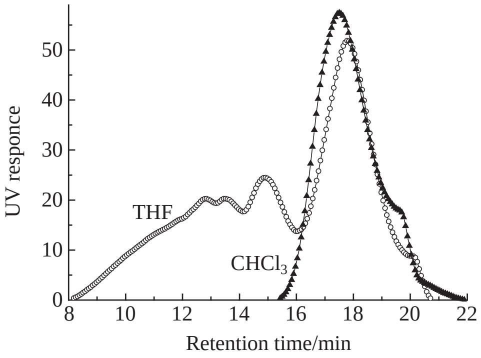


**Figure 2** Elution curves of PIM-1 synthesized at 100 °C for THF and chloroform as eluents.

One can see the MWD maximum shifts to higher $M_w$ with raising the synthesis temperature. The obtained MWD characteristics and, for comparison, some properties of PIM-1 sample prepared by the Budd method[1] are given in Table S1. Peaks on SEC chromatograms and calculated MWD curves represent the sums of linear chains and cyclic oligomers. Therefore, calculated total PDI values may be much higher than it is expected by the Flory distribution. Additional inaccuracies in PDI and $M_w$ measurements are caused by the calibration procedure using PS standards instead of narrow fractions of studied polymer and the band broadening inherent to liquid chromatography. Hydrodynamic sizes of the linear oligomers and their cyclic analogues are close to each other. So that, in principle, SEC method cannot separate these species. Therefore, for the sake of rough characterization of the main polymer fraction, we have divided chromatograms into two parts: main polymer peak and shoulder corresponding to oligomers. The PDI values of the main peaks are not so far from the ones of the most probable distribution (see Table S1).

To optimize SEC conditions for PIM-1 characterization, two eluents were tested using the same set of columns (two Ultrastyragel HR Linear columns). It is interesting to compare the SEC curves obtained in different solvents (Figure 2). In contrast to chloroform, where the chromatogram reflects size distribution of macromolecules, in THF, supramolecular species of various sizes are observed, which cannot be disrupted in the course of chromatography. Similar features were revealed for all of the studied polymers. Thus, the molecular characterization of the prepared by the new synthetic route PIM-1 samples conducted in this study shows good perspective for its large-scale production. It does not indicate to crosslinking as a side reaction in polycondensation process. By default, most of cyclic oligomers can be separated from a fine-dispersed polymer powder after filtration of the reaction mixture. However, more detailed study should be performed for conclusive proof.

In conclusion, the suggested method is a good alternative to the other known PIM synthesis procedures due to its high efficiency and environmental advantages and would be of interest for large-scale applications.

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*Online Supplementary Materials*

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2016.07.033.

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# Corrigendum

## Synthesis of polymorphic titanium oxide nanoparticles by a rapid gas-phase chemical reaction

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The authors regret having to change the authorship of their published article, *viz.* to remove the names Weidong Liu and Liangchi Zhang from the author list. The authors would like to apologise for any inconvenience caused.