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Poly(silyl ether)s (silyl ether copolymers) *via* hydrosilylation of carbonyl compounds

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Hydrosilylation of carbonyl compounds gives the corresponding silyl ethers in the presence of various catalysts. Previously, transition metals and metal halides, such as Ni, $NiCl_2$, $ZnCl_2$, and H_2PtCl_6, were efficiently used for the hydrosilylation of carbonyls. The hydrosilylation strategy using dicarbonyls (diketones and dialdehydes) or hydroxy ketones with dihydrosilanes was then implemented in polymer production to afford the synthesis of poly(silyl ether)s (PSE)s. The first preparation of PSEs by the Weber group used aromatic α,ω-dicarbonyl, and dihydrosilane catalyzed by transition metal complexes, expensive/low abundance ruthenium, and rhodium, whereas nowadays, inexpensive/high abundance catalysts (Mn, Zn, and Cu) and metal-free catalyst (tris(pentafluorophenyl)borane ($B(C_6F_5)_3$)) have attracted much interest in the synthetic approach toward PSEs. Furthermore, the metal-free catalysts utilized in the hydrosilylation of carbonyls have recently found practical applications in polymer chemistry. Moreover, the chiral PSEs developed by the Zhou group have promising applications in asymmetric catalysis and chiral separation as chiral stationary phases. Particularly, this review focuses on the synthesis of PSEs through various dicarbonyls (or hydroxyl carbonyls) and disilanes. We excluded papers regarding methods involving the polycondensation of diols with dichlorosilanes, diaminosilanes, or dialkoxysilanes and ring-opening polymerization (ROP) of cyclic carbosiloxane.

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Introduction and background

Metal halides such as $NiCl_2$, $ZnC1_2$, or H_2PtCl_6 are efficient catalysts for the hydrosilylation reaction of carbonyl compounds, although the mechanism has not been completely identified.[1,2] Calas and Frainnet's group reported that a metal halide such as $ZnCl_2$, or $NiCl_2$ could be utilized as a catalyst in the hydrosilylation of benzaldehyde with Et_3SiH, resulting in silyl ether disproportionating immediately to dibenzylether and hexaethyldisiloxane under vigorous reaction conditions (high temperatures and long reaction times) (Scheme 1).[3]

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Scheme 1 Silylation of aldehydes with Et_3SiH using $ZnCl_2$ (or Ni) as the catalyst.[3]

Scheme 2 A plausible mechanism proposed by the Ojima group for the hydrosilylation of carbonyl compounds catalyzed by $(Ph_3P)_3RhCl$. Reproduced from ref. 4 with permission from Elsevier, copyright 1975.

It should be noted that the disproportionation of the silyl ether product was frequently observed in the case of aldehydes under the reaction conditions given above.

Ojima et al. first employed a rhodium(I) complex ($(Ph_3P)_3RhCl$) as a catalyst in the hydrosilylation of a variety of carbonyl compounds (simple aldehydes and ketones, α-diketones, α,β-unsaturated carbonyl compounds, *etc.*) under mild reaction conditions (Scheme 2).[4] The authors selected mono-, di-, and tri-hydrosilanes as organosilane sources for the hydrosilylation of carbonyl compounds. The same group also noted that no disproportionation was detected when the rhodium(I) complex was utilized in the hydrosilylation of compounds; for example, with benzaldehyde, only benzyloxysilane was obtained in high yields.

Scheme 3 (A) $B(C_6F_5)_3$-catalyzed hydrosilylation of carbonyl compounds using R_3SiH. R^1 and R^2 were not indicated. Reproduced from ref. 5 with permission from American Chemical Society, copyright 1996 and ref. 6 with permission from the Royal Chemical Society, copyright 2015, (B) reductive etherification reaction (RER) of carbonyl compounds using PMHS catalyzed by $B(C_6F_5)_3$. Reproduced from ref. 7 with permission from Elsevier, copyright 2004.

Piers group for the first time presented the hydrosilylation of aromatic aldehydes, ketones, and esters at room temperature in the presence of 1–4 mol% of tris(pentafluorophenyl) borane ($B(C_6F_5)_3$) and 1 equiv. of triphenyl silane (Ph_3SiH). Scheme 3A illustrates the reaction mechanism for the $B(C_6F_5)_3$-catalyzed hydrosilylation of ketones.[5,6] They also highlighted that limiting the silane reagent to 1 equiv. was essential for clean reactions since further reduction of the silyl ether or silyl acetal products was observed when excess silane was present. More recently, the Chandrasekhar group reported that an efficient synthesis of symmetrical and unsymmetrical ethers could be achieved by reductive coupling of carbonyl compounds with alkoxysilanes.[7] This reaction is performed using inert polymethylhydrosiloxane (PMHS) (2 equiv.) as the hydride source and $B(C_6F_5)_3$ (1 mol%) as the catalytic activator of the PMHS. They proposed a plausible mechanism for this

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reductive etherification reaction (RER) platform in which coordination of the carbonyl compound with $B(C_6F_5)_3$ is followed by the formation of an acetal intermediate, which abstracts hydride from PMHS and gives the corresponding ether (Scheme 3B).

The hydrosilylation of carbonyl groups in ketones and aldehydes follows the RER mechanism. In the RER protocol, carbonyl compounds in the presence of silane and a Brønsted or Lewis acid catalyst afford the synthesis of symmetric and unsymmetrical ethers.[8–28] However, the silyl ether is produced rather than the corresponding ether in the hydrosilylation. Notably, both mechanisms seem to cover the competing reaction pathways.

More interestingly, triethylsilane (Et_3SiH) with $B(C_6F_5)_3$ also reduces ethers (dialkyl and aryl alkyl ethers) to the corresponding alkanes under ambient conditions.[29] Various research groups have employed the silane–$B(C_6F_5)_3$ combination in the reduction of carbonyl to alkanes (deoxygenation) as well.[30,31] The use of an R_3SiH Lewis acid catalyst in combination with $B(C_6F_5)_3$ in both silyl ether and alkyl ether syntheses using carbonyl compounds seems intriguing and unusual.

Synthesis of poly(silyl ether)s (PSEs) *via* hydrosilylation of carbonyl compounds

PSEs, similar to poly(siloxane)s, are high-performance materials, which demonstrate high thermal stability, but they have low hydrolytic stability due to acid-catalyzed hydrolysis of their silyl ether (Si–O–C) backbone. PSEs as high-performance materials can be employed as elastomeric products, gas-permeable membranes, and biocompatible coatings for commodity applications.[32,33] On the other hand, the labile silyl ether connections of PSEs enable environmental and biomedical advantages and applications.[34]

PSEs have been prepared *via* several routes involving the polycondensation reaction and ring-opening polymerization (ROP) (Table 1). The polycondensation reaction occurs between dialkoxysilane and α,ω-diol. As an alternative, dichlorosilane cannot be used with α,ω-diol due to the formation of HCl, which leads to the hydrolysis of the silyl ether linkage.[35] PSE has also been synthesized by acid-catalyzed ROP of 1-oxa-2-silacyclopentane, which has been achieved by platinum-catalyzed intramolecular hydrosilylation of dimethylsilyl allyl ether.[36] Following the ROP methodology, PSE has been produced by the reaction of bis(glycidyl) ether with dichlorosilane. In this route, tetra *n*-butyl ammonium chloride catalyzes the reaction, and the chloride nucleophile attacking the oxirane ring results in ring-opening and the formation of chloromethyl and a secondary alkoxide group. The polymerization occurs when a secondary alkoxide sequentially reacts with the silyl halide to produce a silyl ether linkage and regenerate the tetra *n*-butyl ammonium chloride catalyst.[37–39] Weber and coworkers carried out seminal work on the hydrosilylation of carbonyl compounds catalyzed by transition metal complexes, including ruthenium and rhodium, to result in the synthesis of PSEs.[40] In this protocol, 1,4-diacetyldiphenyl ether, 1,4-diacetylbenzene, or terephthalaldehyde with 1,3-tetramethyldisiloxane were copolymerized using dihydridocarbonyltris(triphenylphosphine)ruthenium $(Ph_3P)_2RuH_2CO$ catalyst in toluene at 100 °C for 12 h (Scheme 4). The molecular weight (M_w) and dispersity ($Đ$) of the polymers were determined by GPC and found in the range of 93 to 48 kDa and 3.52–2.74, respectively. The authors carried out the methanolysis reaction of PSEs and observed significant differences in stability toward methanolysis. The PSE structure having the primary C linked to the O atom is unstable upon precipitation in methanol at room temperature. However, PSEs with a secondary C bonded to the O atom display more resis-

Table 1 Developed approaches for the synthesis of PSEs

Methods for the synthesis of PSEs	Compounds	Structure of PSE	Ref.
Polycondensation	Dichlorosilane, diaminosilanes or dialkoxysilane and diol		35
Ring-opening polymerization	1-Oxa-2-silacyclopentane		36
Hydrosilylation polymerization	Bis(glycidyl) ether and dihalosilane		38
	Aldehyde (or ketone) and silane		40
Hydrosilylation and dehydrogenative cross-coupling polymerization	Hydroxy-aldehyde or -ketone and silane		52
Dehydrogenative cross-coupling polymerization	Diol and silane		56

Scheme 4 Synthesis of PSE using terephthalaldehyde and 1,3-tetramethyldisiloxane catalyzed by ruthenium. Reproduced from ref. 40 with permission from the American Chemical Society, copyright 1998.

Scheme 5 PSE synthesis from phenanthrene-9,10-dione and 1,9-dihydridodecamethylpentasiloxane. Reproduced from ref. 41 with permission from the American Chemical Society, copyright 2001.

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tance to methanolysis. The authors indicated that the PSEs obtained in this work might similarly offer controlled degradation upon hydrolysis. The authors also noted that the PSEs are thermally stable up to almost 300 °C.

As an extension of this work, the Weber group reported the Ru-catalyzed hydrosilylation polymerization of *o*-quinones with α,ω-dihydridooligodimethylsiloxane (ODMS) to yield high-molecular-weight PSEs (M_n varies in the range of 8.6–41 kDa) (Scheme 5).[41] The polymerization was carried out in bulk using activated $(Ph_3P)_2RuH_2CO$ as a catalyst under an argon atmosphere at 125 °C for 18 h. As expected, the T_gs of the polymers decreased in parallel to the increasing number of repeating units (n) of ODMS. When the n of the ODMS is 6, the T_g of the PSE was found to be −100 °C, which is fairly close to the T_g of polydimethylsiloxane (−125 °C).

In the following work, aliphatic ω-dimethylsilyloxy ketones or aliphatic a,ω-diketones with ODMS were polymerized in bulk at 125 °C for 18 h using the abovementioned Ru catalyst to yield unsymmetrical and symmetrical PSEs, respectively (Scheme 6).[42]

The M_ws determined by GPC display PSEs with broad molecular weights ranging from 4.5 to 85.5 kDa. The T_gs for PSEs display similar behavior to that described previously for PSEs with aromatic precursors. A similar behavior was observed if the C atom of the Si–O–C linkage is secondary; PSEs having this structure are considerably more resistant to hydrolysis and methanolysis than if it is primary.

Scheme 6 Preparation of unsymmetrical PSE using 5-dimethylsilyloxy-2-pentanone using Ru catalyst at 125 °C for 18 h. Reproduced from ref. 42 with permission from the American Chemical Society, copyright 2002.

A similar strategy was also applied to the synthesis of PSEs starting from dimethylsilyloxyaryl ketones or aldehydes using an activated Ru catalyst under the abovementioned reaction conditions (Scheme 7).[43]

It should be noted here that the hydrosilylation polymerization gave high-molecular-weight PSEs (up to M_w = 168 kDa) with high isolated yields (in the range of 80–85%). The Weber group noticed that the T_gs of PSEs decrease as the number of dimethylsiloxane units between the aromatic moieties increases.

The Oro group reported the rhodium-catalyzed synthesis of PSEs.[44] They first showed that rhodium(I)-N-heterocyclic carbenes (Rh(I)-NHCs) with labile NHCs are very efficient and selective catalysts for alkyne hydrosilylation[45] and hydrogen transfer hydrogenation.[46] They used a Rh(COD)(2-methoxyethyl-NHC-$(CH_2)_3Si(OiPr_3)_3$)Br homogenous catalyst in the hydrosilylation of terephthalaldehyde with 1,1,3,3,5,5-hexamethyltrisiloxane (hexMTS) in dioxane at 110 °C for 4 days (Scheme 8) (Table 1). They obtained the final PSE as a yellow oil (M_w = 5.2 kDa and $Đ$ = 1.7) in quantitative yield. As a second step, authors prepared a heterogeneous catalyst immobilizing the Rh(COD)(2-methoxyethyl-NHC-$(CH_2)_3Si(OiPr_3)_3$)Br on a mobile crystalline material-41 (MCM-41) and employed it in similar reaction conditions to those given above. The PSE was obtained with bimodal distribution containing two portions: 22% of total mass with M_w = 94 kDa ($Đ$ = 1.6) and 78% of total mass with M_w = 7.4 kDa ($Đ$ = 1.5).

Scheme 7 PSE synthesis from hydrosilylation of 4-dimethylsilyloxyacetophenone. Reproduced from ref. 43 with permission from Elsevier, copyright 2000.

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Scheme 8 Hydrosilylation of terephthalaldehyde with hexMTS using Rh(COD)(2-methoxyethyl-NHC-$(CH_2)_3Si(OiPr_3)_3$)Br homogenous catalyst. Reproduced from ref. 44 with permission from John Wiley and Sons, copyright 2013.

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In the following work, the Oro group changed 2-methoxy ethyl to 2,6-diisopropylphenyl in the Rh-NHC complex, then immobilized it in mesoporous materials, such as MCM-41 and KIT-6, and finally utilized the immobilized catalysts in the preparation of PSE by catalytic hydrosilylation under the same reaction conditions as those mentioned above.[47] These heterogeneous catalyst systems gave PSEs with high molecular weights (M_w = 2.61 × 10^6 and M_w = 4.43 × 10^5 g mol^{-1}) for those immobilized on MCM-41 and KIT-6, respectively.

Recently, the Cui group utilized the zwitterionic heteroscopionate zinc hydrido complex (LZnH) as a cheaper and less toxic catalyst compared to traditional rhodium and ruthenium catalysts.[48] The authors employed the LZnH catalyst in the hydrosilylation of terephthalaldehyde, isophthalaldehyde, and phthalaldehyde using diphenylsilane (DPS) to afford PSEs (Scheme 9). The polymerizations were carried out at 40 °C in THF under N_2 in the range of 24 to 72 h. PSEs with high molecular weights (M_n = 20.3–17.6 kDa; $Đ$ = 2.35–2.60) were achieved when terephthalaldehyde and isophthalaldehyde were used as monomers with DPS in the polymerization. Nevertheless, phthalaldehyde afforded only a seven-membered cyclic silyl ether.

Du and coworkers presented a manganese–salen (MnN (salen-3,5-*tert*-Bu_2)) catalyst as a cheap and nontoxic metal for hydrosilylation of dicarbonyl compounds as well as dehydrogenative cross-coupling of diols to yield PSEs (Scheme 10).[49] The authors also employed compounds containing both carbonyl and hydroxyl functionalities *via* a combination of hydrosilylation and dehydrogenative cross-coupling mechanisms for PSE production. The polymerization reactions of dicarbonyls with DPS were carried out using the manganese catalyst at the reflux temperature of high boiling solvents for longer reaction times (12–48 h) to produce PSEs with rather low molecular weights ranging from M_n = 1.8 to 2.4 kDa ($Đ$ = 1.73–1.88) in low yields. However, analogous structures of diols compared to dicarbonyls gave moderately high-molecular-weight PSEs (M_n = 9–15 kDa, $Đ$ = 1.41–2.38) with high yields. This may be ascribed to the stronger nucleophilicity of hydroxyl than that

Scheme 9 The plausible mechanism for the polymerization of aromatic dialdehydes and DPS in the presence of LZnH. Reproduced from ref. 48 with permission from John Wiley and Sons, copyright 2017.

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Scheme 10 A plausible mechanism for the synthesis of PSEs from dicarbonyl and DPS using a manganese–salen (MnN(salen-3,5-*tert*-Bu_2)) catalyst. Reproduced from ref. 49 with permission from the American Chemical Society, copyright 2017.

of carbonyl. When *p*-hydroxybenzaldehyde was selected as a mixed monomer to react with DPS, a PSE with M_n = 3.8 kDa ($Đ$ = 1.73) was achieved under similar reaction conditions.

Scheme 11 LZnH and $B(C_6F_5)_3$ pair as synergistic catalysts employed in the hydrosilylation of HMF. Reproduced from ref. 51 with permission from John Wiley and Sons, copyright 2019.

More recently, extending this system (hydrosilylation and dehydrogenative cross-coupling polymerization) to the furan-based monomers, 5-hydroxymethylfurfural (HMF), 2,5-bis-(hydroxymethyl)furan, 2,5-diformylfuran, and 5,5′-[oxybis-(methylene)] di(2-furaldehyde), derived from biorenewable sources, Du and coworkers obtained a series of PSEs with high molecular weight (up to M_n = 25 kDa) under similar reaction conditions to those given above.[50]

Cui and coworkers exploited a previously mentioned HMF monomer as a renewable source with DPS or methyl phenyl silane in the presence of a new pair of catalysts, $B(C_6F_5)_3$ and the heteroscorpionate zinc hydride complex LZnH (L = $(^{Me}Pz)_2CP(Ph)_2NPh$, ^{Me}Pz = 3,5-dimethylpyrazolyl), to result in the corresponding PSE (Scheme 11).[51] When DPS was employed as a comonomer with a ratio of HMF : DPS : LZnH = 100 : 100 : 1, in toluene at room temperature for 24 h, followed by 48 h at 40 °C, a PSE was obtained with M_w = 12.2 kDa and $Đ$ = 1.23. On increasing the ratio of HMF : DPS : LZnH to 200 : 200 : 1, the M_w of the PSE increased to 19.8 kDa with $Đ$ = 1.31. Similar results were observed in the case of the methylphenyl silane, suggesting that both polymerizations proceeded in a controlled fashion.

The bio-based building block HMF (or vanillin) and disilanes (DPS, methylphenyl silane, or diethylsilane) were polymerized using Pt(II) complexes as catalysts in 2-methyl tetrahydrofuran (MeTHF) at room temperature for 24 h and 50 °C for 4 h to yield the corresponding PSEs.[52] When HMF and DPS were polymerized, a catalytic loading of 500 ppm of [Pt]Me was sufficient to obtain a PSE with high molecular weight (M_w = 57.5 kDa and $Đ$ = 3.5) and high yield (Scheme 12).

Recently, Li and Hawker utilized only $B(C_6F_5)_3$ in a metal-free catalyst concept for the preparation of PSEs using aryl-substituted α-diketone and bis(silane) monomers under mild reaction conditions (Scheme 13).[53]

Notably, considering the monomers benzil and 1,4-bis(dimethylsilyl)benzene, 0.5 mol% of $B(C_6F_5)_3$ catalyst loading and equimolar reaction conditions in $CHCl_3$ and toluene produced PSEs with M_w = 47 kDa ($Đ$ = 1.8) and M_w = 98 kDa ($Đ$ = 1.8) in 80% yield, respectively. The authors confirmed that a cyclic dimer was detected in 15% yield in all polymerization systems.

Scheme 12 Preparation of PSE containing HMF and DPS using [Pt]Me catalyst in MeTHF. Reproduced from ref. 52 with permission from John Wiley and Sons, copyright 2022.

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Scheme 13 Preparation of a PSE using benzil, 1,4-bis-(dimethylsilyl)benzene, and $B(C_6F_5)_3$ in $CHCl_3$ or toluene. Reproduced from ref. 53 with permission from American Chemical Society, copyright 2019.

Scheme 14 Synthesis of chiral PSE utilizing monomers 1,1,3,3-tetramethyldisiloxane and 4,4′-diacetylbiphenyl in the presence of copper(II) cyclohexanebutyrate/**L** catalyst in *tert*-butyl methyl ether at 30 °C for 24 h. Reproduced from ref. 54 with permission from the American Chemical Society, copyright 2020.

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Moreover, methanolysis and hydrolysis of the selected PSEs were monitored as a function of time against changes in the M_n values by GPC. The PSEs containing silphenylene units demonstrated no change in M_n for up to 15 days in methanolysis. However, the M_n of the siloxane-based PSE decreased to half of the initial molecular weight after 15 days. Moreover, both PSEs with silphenylene and siloxane units were stable in the presence of trimethylamine over the same time. As expected, both polymers are prone to acidic hydrolysis while exhibiting a sharp decrease in M_n values to complete degradation within 12 h and 7 days for siloxane- and silphenylene-based PSEs, respectively.

Chiral PSEs have been prepared using a wide diversity of dicarbonyls and disilanes in the presence of CuH catalysts in various solvents and temperatures.[54] The Zhou group employed 1,1,3,3-tetramethyldisiloxane and 4,4′-diacetylbiphenyl as model monomers and investigated the effects of solvents, copper precursors, and bisphosphine ligands, both on the reactivity and diastereoselectivity for optimization of the reaction conditions. As a result, model monomers were polymerized utilizing the copper(II) cyclohexanebutyrate/**L1** catalyst in *tert*-butyl methyl ether at 30 °C for 24 h, and therefore, the resultant PSE was achieved with high yield, moderately high molecular weight (M_n = 11.8 kDa, $Đ$ = 2.39) and excellent stereoselectivity (up to 99% ee and 96 : 4 dl/*meso*) (Scheme 14).

The authors claimed that the enantiopure PSEs with good thermal properties might have a potential application in chiral separation, and the PSEs with heteroaromatic rings play a promising role in heterogeneous asymmetric catalysis. In the following work, the Zhou group employed the CuH-catalyzed consecutive hydrosilylation/dehydrogenative cross-coupling polymerization of hydroxy ketones and dihydrosilanes to afford chiral PSEs.[55]

Conclusion and outlook

As a first approach, the Weber group employed transition metal catalysts (Ru/Rh salts) in the synthesis of PSEs using dicarbonyl and dihydrosilane, while they benefited from the work of the Ojima group. However, the experienced vigorous reaction conditions, and the low abundance and high cost of transition metal catalysts (Ru/Rh), pushed the chemists to develop new catalysts. In recent years, based on the hydrosilylation reaction, chemists have developed novel metal catalysts that are cheap and highly abundant. Zinc hydride complex, manganese–salen complex, zinc hydride–$B(C_6F_5)_3$ complex, Pt complex, and copper complex were developed as catalysts in recent years. These catalysts allowed the synthesis of PSEs under relatively mild conditions. Of the catalysts, Mn and Pt

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complexes should be considered biocompatible catalysts and can be employed for the synthesis of PSEs from biorenewable feedstocks. Moreover, increasing interest in mild and metal-free techniques for the synthesis of small organic molecules and polymers led to the development of various metal-free catalysts. From this perspective, $B(C_6F_5)_3$ as a metal-free catalyst has been widely used both for hydrosilylation coupling reactions and PSE synthesis under mild conditions.

Since PSEs that contain Si–O–C bonds are more susceptible to acid- or base-catalyzed hydrolysis and methanolysis compared to polysiloxanes with Si–O–Si bonds, this feature makes them attractive materials for biomedical and environmental applications. Notably, the degradation behavior of PSEs, besides the thermomechanical properties, can be modified by varying the substituent groups on the Si and/or C atoms on the backbone of the PSEs and by copolymerization with other polymer chains. Thus, the hydrolytic lability of the Si–O–C linkage of PSEs makes them highly attractive for use in drug delivery systems. The PSEs achieved from biomass (furan monomers) can also undergo hydrolytic degradation and completely degrade under acidic conditions to yield the corresponding furan diol and silanediol.

Additionally, PSEs have found applications in the aerospace industry as CO_2-philic polymer membranes, reprocessable and degradable thermosets, and for preparing dielectric or fluorescent materials and elastomeric materials. Enantiomerically enriched PSEs with good thermal stability are promising for applications in chiral separations as chiral stationary phases.

Conflicts of interest

There are no conflicts to declare.

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