Comparative assessment of hydrocarbon separation performance of bulky poly(urethane-urea)s toward rubbery membranes

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ABSTRACT

In the present study, two series of poly (urethane urea)s (PUUs) membranes containing aromatic and aliphatic side chains with different sizes were used for separation of higher hydrocarbons from methane. Fourier-transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), fractional free volume (FFV) estimation, and gas permeation measurements (CH4, C2H6, C3H8) were done to characterize the membranes. Bulkier or longer side chains in aromatic and aliphatic substituted PUUs provided enhanced phase separation, lower glass transition temperature and higher gas permeability. Fractional free volume (FFV) as a significant factor controlling gas separation had a reverse trend in both series by increasing the size of side chains. The main findings confirmed the capability of higher phase separated PUUs for hydrocarbon separation. The highest permeability and selectivity was obtained by the longest side chain based PUU with propane permeability of 186 barrer and propane/methane selectivity of 6.51.

1. Introduction

Natural gas typically contains methane as the major constituent besides ethane, propane, butane and other higher hydrocarbons in lesser amounts and some impurities such as water, nitrogen, CO2 and H2S. Some treatment of natural gas is necessary before its transfer to the pipeline. Separation of heavy hydrocarbons from natural gas is required for some purposes like recovering valuable heavy hydrocarbons as chemical feedstocks and avoiding condensation during transportation to prevent softening plastic pipelines (Baker and Lokhandwala, 2008; Talakesh et al., 2012; Ilinitych et al., 1992; Khosravi and Sadeghi, 2013; Khosravi et al., 2014). Polymeric gas separation membranes possess economic benefits due to proper intrinsic specifications and processing facility (Ilinitych et al., 1992; Khosravi and Sadeghi, 2013; Zhu et al., 2018; Molino et al., 2013; Kang et al., 2017; Bisoi et al., 2017). Considerable efforts have been done to prepare high performance polymeric membranes for gas separation up to now (Pouranaghabshand Isfahani et al., 2018; Galizia et al., 2017; Dong et al., 2013; Akbarian et al., 2018; Wang et al., 2021; Li et al., 2016). Based on the solution-diffusion mechanism of gas separation (Bandehal et al., 2020; Feng et al., 2019; Sanaeepur et al., 2016), it is well-known that solubility selectivity is dominant for rubbery membranes, while gas separation is governed predominately by diffusivity contrast through glassy ones. Literature implies that rubbery polymers including polyurethane membranes are eligible for separation of higher hydrocarbons from methane through solubility-controlled selectivity. Rubbery polymers with lower glass transition temperatures are preferred for this separation (Javaid, 2005; Yampolskii et al., 2006; Semenova, 2004; Scholes et al., 2012). Several polymeric membranes have been studied for separation of higher hydrocarbons including poly (dimethyl siloxane) (PDMS), poly (octyl methyl siloxane) (POMS) and poly (1-trimethylsilyl-1-propyne) (PTMSP) membranes, silicate membranes, cis-polypentenamer (cis-PMM), poly [1-phenyl-2-[(trimethylsilyl)phenyl]acetylene] (PTMSPDA), poly (4-methyl-2-pentene) (PMP), poly (1-phenyl-1-propyne) (PPP), and polyurethanes (Pus) with various microstructures (Arruebo et al., 2001; Schultz and Peinemann, 1996; Starannikova et al., 2006; Pinnau and He, 2004; Toy et al., 2000).

Among rubbery membranes, PUs have indicated comparable capability for C2H6/CH4 and C3H8/CH4 separations (Khosravi and Sadeghi, 2013; Khosravi et al., 2014; Tirouni et al., 2015). Polyurethanes possess complex and multi block structure containing hard and soft domains. Soft segments are usually flexible consisting of polyol (polyether or polyester) while hard domains consist of urethane or urea linkages generated by reacting diisocyanate and diol or diamine chain
extender. Micro-phase separation occurring in polyurethane affects its physical and gas separation behavior (Halim et al., 2014; Sadeghi et al., 2018; Pournaghshband Isfahani et al., 2017). The results of previous studies suggest that an improved phase separation warrants higher permeability, since the soft domains of PUs dominate the gas transport (Shahrooz et al., 2016). Additionally, the presence of urea linkages in the structure favors the phase separation degree (Sadeghi et al., 2010). Beside phase separation, other factors including microstructure, molecular weight, fractional free volume (FFV), composition, chain flexibility, interchain interactions, and diffusion barriers affect the gas separation properties of polymeric membranes (Khosravi and Sadeghi, 2013; Pournaghshband Isfahani et al., 2016a, 2018; Fakhar et al., 2019a, 2019b; Mozaffari et al., 2017; Luo et al., 2016; Dai et al., 2005; Qiu et al., 2007; Pinnau et al., 2004; Nagel et al., 2002). Khosravi et al. (Khosravi and Sadeghi, 2013) studied the influence of different polyols (Qiu et al., 2007; Pinnau et al., 2004; Nagel et al., 2002). Khosravi et al. (Shahrooz et al., 2016). Additionally, the presence of urea linkages in the structure favors the phase separation degree (Sadeghi et al., 2010).

Separation of hydrocarbons like propane with high condensability from methane are best-done by rubbery sorption-selective membranes. Here, new polyurethane membranes were served for this purpose. We aim to elucidate the structure-property relations of the PUs membranes and their comparative potential for hydrocarbon separation. Hard domains considered as impermeable regions for gas transport and mainly responsible for the mechanical strength of PU (Fakhar et al., 2020). To investigate the influence of hard segment design on gas transport, polyurethanes containing the same soft segment and various hard segments (two types of diisocyanates and two series of side chain based-chain extenders) were studied (Fakhar et al., 2019a, 2019b). The first PUU series contained aromatic side chain substituted chain extenders with different ring numbers, while the second class were based on alkyl side chain substituted chain extenders with different-length aliphatic side chains (Fakhar et al., 2019a, 2019b). This study investigates the novel PUU membranes for separation of heavy hydrocarbons from methane compared to other rubbery membranes.

2. Experimental

2.1. Materials

Cyanuric Chloride (CC), aniline and α-naphthylamine (to prepare aromatic chain extenders), hexylamine, dodecylamine and octadecylamine (to amine for aliphatichain extenders), sodium hydrogen carbonate, and hydrazine were purchased from Merck to synthesize three bulky chain extenders with different side chain-length. Aceton, acetic acid, and dichloromethane were provided from Ameretah shimi pharmaceutic. Poly (tetramethylene glycol) (PTMG, Mw: 2000 g/mol) was purchased from Arak Petrochemical. Dibutylendilaurate (DBTDL) as a catalyst, isophorone diisocyanate (IPDI), hexamethylene diisocyanate (HDI), dehydrated dimethyl acetamide (DMAc) and dimethyl formamide (DMF) were supplied by Merck. Butanediol (BDO) and butanediol-diisocyanate (BDA) were purchased from Sigma-Aldrich and dried over 4 Å molecular sieves.

2.2. Polyurethane synthesis

First, a two-step reaction was used to synthesis two categories of diamine chain extenders; one contains aromatic and the other contains aliphatic side chains. As the first step, substitution of one chlorine atom on the triazine ring of CC by an aromatic or aliphatic-based amines was done. Afterwards, the two residual chlorines of the triazine ring was substituted through a reaction with hydrazine. Through this procedure, two aromatic side chain- and three aliphatic side chain-based chain extenders were synthesized based on the procedures as mentioned in our previous studies, in details (Fakhar et al., 2019a, 2019b). The chemical structures of all synthesized chain extenders for preparing two series of bulky PUUs are depicted in Scheme S1.

A two-step polymerization method was applied to synthesize all polymers. The dried PTMG under vacuum was used with excess of IPDI or HDI (PTMG: diisocyanate 1:3 M ratio) at 80 °C under nitrogen for 2 h with some DMAC as solvent. DBTDL was the catalyst for the reaction. Then, the obtained –NCO terminated pre-polymer was chain extended by adding the pre-synthesized chain extenders to the reaction medium at ambient temperature. The temperature was raised to 70 °C and the reaction was kept under nitrogen for 24 h. The post reaction of the product was performed in an oven at 95 °C overnight. The molar ratio of NCO: OH was 1:1 to gain a linear polymer, and 1:3:2 M ratio of PTMG: diisocyanate: chain extender was used.

Different sample notations of the prepared polymers were reported in Table 1. In addition, Scheme S2 depicts the chemical structures of all synthesized bulky PUUs.

2.3. Membrane preparation and characterization

A procedure of casting solutions of 10 wt% polymer in DMF followed by solvent evaporation at 60 °C for 24 h in an oven followed by 24 h in vacuum was served for membrane preparation. The thickness of prepared membranes was measured around 100 μm by a digital micrometer. ATR-FTIR and DSC was performed on the membranes and the results were reported in our previous studies (Fakhar et al., 2019a, 2019b). Solubility parameters of soft and different hard segments of various polyurethanes were also reported in the previous studies (Fakhar et al., 2019a, 2019b).

Pure hydrocarbon (CH₄, C₂H₆, and C₃H₈) permeation measurements of the membranes were performed at 30 °C and 1 bar. Gas separation tests were done three times for each membrane on three samples of the same polyurethane to report the average results.

| Sample | Diisocyanate | Chain extender |
|--------|--------------|----------------|
| Reference polyurethanes | PU | IPDI | 1,4-Butanediol (BDO) |
| | PUU | IPDI | 1,4-Butanediolamine (BDA) |
| Aromatic side chain based PUUs | AI-PUU | IPDI | Aniline-based |
| | NH-PUU | IPDI | Naphthylamine-based |
| | HI-PUU | IPDI | Hexylamine-based |
| | DI-PUU | IPDI | Dodecylamine-based |
| | OH-PUU | IPDI | Octadecylamine-based |
| Aliphatic side chain based PUUs | HH-PUU | IPDI | Hexylamine-based |
| | HD-PUU | IPDI | Dodecylamine-based |
| | OH-PUU | IPDI | Octadecylamine-based |
3. Results and discussion

3.1. Phase separation extent and FFV values

Fig. 1 shows the FTIR spectra of the bulkiest and longest side chain-based PUUs of two categories for two types of diisocyanate. The characteristic peaks for polyurethanes are observed in all spectra including C=O stretching at 1600-1800 cm⁻¹, NH stretching at around 3300 cm⁻¹, the C–O–C ether at 1110 cm⁻¹, the CH₂ signals of PTMG at 2940 and 2856 cm⁻¹. Additionally, the completion of the reaction was confirmed by the disappearance of the NCO peak at 2250 cm⁻¹ (Fakhar et al., 2019a, 2019b).

Two types of hydrogen bonding can occur in polyurethanes including hydrogen bonding between NH and C=O groups of the hard domains which favors phase separation between hard and soft domains, and the interaction between soft segments and the NH groups of hard segments (Chattopadhyay et al., 2005; Miller et al., 1985). Hydrogen bonding index (HBI), the ratio of absorbance of bonded to free carbonyl groups from FTIR spectra, quantifies the phase segregation extent. Higher HBI values indicate higher segregation between soft and hard phases (Pournaghshband Isfahani et al., 2016b, 2016c). The deconvolution data (using OriginPro) of the free and bonded carbonyl groups are presented in Fig. S1 for the bulkiest and longest side chain-based PUUs. HBI and FFV values of the PUUs are depicted in Fig. 2. These values along with glass transition temperature (T_g) of soft segments and solubility parameters of both domains of PUUs are reported in Table S1.

Fig. 2 and Table S1 indicate that phase separation (or HBI) in both series of synthesized PUs increase by the size of the side chains (bulkier or longer side chains) attached on hard domains. Additionally, HDI-based PUUs in both series possess a higher phase separation degree compared to IPDI-based ones. The decreased T_g of soft segments is another evidence for enhanced phase separation. The solubility parameter difference between soft and hard segments for the aromatic side chain-based PUUs for both types of diisocyanates increased as a bulkier substituent was used which induces stronger phase separation (Miller et al., 1985). For the aliphatic side chain-based PUUs, a lower solubility parameter difference between soft and hard segments was obtained by lengthening the aliphatic side chain. Due to the incompatibility of the aliphatic substituents with the main chain of hard domains (see their solubility parameters in Table S1), phase separation between main and side chain parts in the hard domains would be also propable (Hiller et al., 2004; Hugger et al., 2004). As interpreted in details in our previous study (Fakhar et al., 2019b), the side chains presenting a low surface energy can shield the main chains of hard segments which results in more segregation between soft and hard phases (Tan et al., 2004a, 2004b, 2005). This shielding mechanism would decrease accessible NH groups to interact with the soft segment favoring phase separation. Additionally, compatibility of the alkyl side chains with the soft phase is clear based on their similar solubility parameters. This likely give rise to creation of more pure soft and hard phases.

Bulking up and lengthening the side chains in both series led to an increase and decrease in FFV, respectively (Fig. 2 and Table S1). The higher FFV along with more phase separation is a typical observation as seen by others (Wang et al., 2003; Amanti et al., 2014). For the second series, longer side chains resulted in lower FFV values, despite the higher HBI values. Reduction in FFV values with longer side chains would strengthen the shielding mechanism, mentioned before.

HDI-based PUUs gives higher FFV values compared to IPDI-based ones with the same chain extender. This is consistent with the usual behavior of higher FFV values for PUs with higher phase segregation.

3.2. Gas permeation properties

The CH₄, C₂H₆, and C₃H₈ permeabilities, C₂H₆/CH₄ and C₃H₈/CH₄ selectivities are reported in Table 1 at 30 °C and 1 bar. To ensure that the selected pressure is below the plasticizing point, N₂ permeability before and after each hydrocarbon transport measurement was measured. No noticeable change was seen in N₂ permeability after every measurement (Khosravi et al., 2014; Tirouni et al., 2015). Based on Table 2, the growth in permeability through aromatic and alkyl side chain substituted PUUs is evident by bulking up and lengthening the side chain. The enhanced permeability of the bulkier PUUs arises from higher phase separation and higher FFV values. More shielded hard domains, higher plasticization effect, higher purity of soft and hard domains along with higher HBI all explain the enhanced permeability by lengthening the aliphatic side chains. Higher phase separation results in a more rubbery character of PU. The increased rubbery behavior gives rise to increased permeability of more condensable gases (Khosravi and Sadeghi, 2013). For all PUs the permeability increased as the number of carbons in the alkanes increased: C₃H₈ > C₂H₆ > CH₄. Since gas separation through rubbery polymers such as PUs is solubility-controlled, propane with the highest critical temperature among the studied hydrocarbons presents the highest permeability (the critical temperatures...
of the studied alkanes decrease in the following order: propane (231.1 K) > ethane (184.5 K) > methane (111.7 K) (Semenova, 2004). Considering the obtained C₂H₆/C₄H₁₀ and C₃H₈/C₄H₁₀ selectivities the bulkier or longer side chain-based PUUs provide higher selectivities along with higher permeability. The Higher phase separation obtained by the bulkier or longer substituted PUU enhances the rubbery character of polyurethanes favoring easier separation of more condensable molecules from molecules with lower critical temperatures. Enhanced selectivity in C₂H₆/C₄H₁₀ and C₃H₈/C₄H₁₀ separations by an increase in rubbery property of polyurethanes was also seen by Khosravi et al. (Khosravi and Sadeghi, 2013). Also, lengthening the side chains with hydrocarbon nature enhances their structural similarity to propane molecules which provides higher C₂H₆/C₄H₁₀ selectivity. The simultaneous increased permeability and selectivity by longer side chain-based PUUs confirms the higher purity of the domains which facilitates the interaction of aliphatic side chains and soft domains of polyurethane with the alkanes. In addition, HDI-based PUUs presented higher permeability and selectivity compared to IPDI-based ones for the same chain extender due to improved phase separation. The highest hydrocarbon separation was obtained by PUU-O-H as the longest side chain based-PUU containing higher phase separation, higher similarity of side chain with hydrocarbons and more pure domains (166% and 43% improvement in C₃H₈ permeability and C₂H₆/C₄H₁₀ selectivity compared to linear PUU).

The increased permeability and selectivity through both series of PUUs is a considerable effect for their potential in hydrocarbon separation.

Diffusivity and solubility coefficients, and diffusivity and sorption selectivities for the prepared membranes are presented in Table 3.

Based on Table 3, bulkier or longer side chain-based PUUs with enhanced phase separation result in higher diffusivity coefficients due to enhanced chain mobility. The increase in gas diffusivity without a decrease in diffusivity selectivity through bulkier side chain-based PUUs is probably due to the screening character of the bulky side chains. For the second series of PUUs, plasticizing effect of aliphatic side chains favors diffusivity and decreased FFV is in favor of diffusivity selectivity through longer side chain-based PUUs. Solubility and solubility selectivity increased by bulkier or longer side chain as a result of increased rubbery behavior of PUUs arising from higher phase separated structure. Enhanced similarity between longer side chains and higher hydrocarbons, especially propane is another reason for higher sorption. This
confirms the creation of the domains with higher purity by longer side chain substituted PUUs.

The gas diffusivity versus Lennard-Jones diameter ($d_{LJ}$) and solubility versus Lennard-Jones potential factor ($\epsilon/k$) for all the membranes were depicted in Fig. 3 a and b, respectively ($d_{LJ}$ and $\epsilon/k$ values were adopted from (Semenova, 2004)). Gas diffusivity decreased with Lennard-Jones diameter. A linear correlation between log D and the $d_{LJ}$ was obtained, as seen by others (Pournaghshband Isfahani et al., 2020). Fig. 3 b indicates higher solubility through the membranes for increased $\epsilon/k$. The normalized solubility through both series of membranes (relative to PUU as the reference membrane) as a function of $\epsilon/k$ is shown in Fig. 3c and d. The higher rise in the gas solubility with $\epsilon/k$, confirmeds the dominant role of the enhanced rubbery character compared to linear PUU.

Table 3

| Sample                      | Diffusivity ($\times 10^7$ (cm$^2$/s)) | Solubility ($\times 10^3$ (cm$^3$ (STP)/cm$^3$ poly.cmHg)) | Diffusivity selectivity | Solubility selectivity |
|-----------------------------|----------------------------------------|-----------------------------------------------------------|-------------------------|------------------------|
|                             | CH$_4$ | C$_2$H$_6$ | C$_3$H$_8$ | CH$_4$ | C$_2$H$_6$ | C$_3$H$_8$ | CH$_4$ | C$_2$H$_6$ | C$_3$H$_8$ | CH$_4$ | C$_2$H$_6$ | C$_3$H$_8$ |
| PU                          | 3.05   | 2.5        | 1.68       | 3.92   | 8.14       | 19.09      | 1.22   | 1.81       | 2.08       | 4.87   |
| PUU                         | 3.94   | 3.43       | 2.90       | 3.89   | 9.94       | 24.15      | 1.15   | 1.36       | 2.55       | 6.21   |
| Aromatic side chain based PUUs |         |            |            |         |            |            |         |            |            |        |
| AI-PUU                      | 4.79   | 3.89       | 2.98       | 2.90   | 8.51       | 21.10      | 1.23   | 1.61       | 2.93       | 7.27   |
| AH-PUU                      | 5.93   | 4.80       | 3.41       | 3.67   | 14.31      | 37.5       | 1.24   | 1.74       | 3.90       | 10.22  |
| NI-PUU                      | 4.83   | 3.92       | 3.00       | 2.91   | 9.00       | 22.31      | 1.23   | 1.61       | 3.09       | 7.67   |
| NH-PUU                      | 6.40   | 4.85       | 3.65       | 3.96   | 15.34      | 41.09      | 1.32   | 1.75       | 3.90       | 10.38  |
| Aliphatic side chain based PUUs |        |            |            |         |            |            |         |            |            |        |
| HI-PUU                      | 5.65   | 4.96       | 3.61       | 3.04   | 8.79       | 27.37      | 1.14   | 1.86       | 2.89       | 7.58   |
| HH-PUU                      | 7.02   | 6.05       | 3.84       | 3.55   | 12.17      | 37.44      | 1.16   | 1.97       | 3.42       | 9.75   |
| DI-PUU                      | 5.78   | 5.05       | 3.63       | 3.06   | 9.78       | 27.60      | 1.14   | 1.69       | 3.19       | 9.02   |
| DH-PUU                      | 7.73   | 6.62       | 3.91       | 3.34   | 12.38      | 40.80      | 1.17   | 2.31       | 3.71       | 10.41  |
| OH-PUU                      | 6.58   | 5.38       | 3.86       | 3.19   | 10.4       | 32.76      | 1.22   | 1.70       | 3.26       | 10.27  |

Fig. 3. a) The gas diffusivity versus Lennard-Jones diameter ($d_{LJ}$), b) solubility versus $\epsilon/k$, c and d) normalized solubility of the aromatic and alphabetic side chain-based PUU as a function of $\epsilon/k$.
properties of these membranes to some organosilicon membranes warrants the PUUs’ potential for this application.

Table 4 and 5 indicates the improved percentage for the separation performance by the novel membranes compared to other rubbery membranes (presented in Fig. 4). Since the highest separation performance was obtained by OH-PUU, this comparison was expressed between OH-PUU and other membranes. For organosilicon polymers and various polyurethanes derivated from other studies, the mean values of permeability and selectivity were served. Improved C2H6/CH4 and C3H8/CH4 separation values through OH-PUU is visible compared to almost all samples in Tables 4 and 5. The highest improvement was obtained compared to the other polyurethanes and PDMSTM. Based on Tables 4 and 5, improvement in permeability can be seen in some cases, too.

4. Conclusions

The intention of this study was to compare the capability of novel PUUs for hydrocarbon separation with other rubbery membranes. Two series of PUUs containing bulky chain extenders based on aromatic and aliphatic side chains were synthesized for this purpose. The main findings indicate a higher phase separation degree between soft and hard domains of the PUUs by bulking up or lengthening the side chains.

Table 4
The improved percentage for C2H6/CH4 separation through OH-PUU compared to other rubbery membranes.

| Sample        | C2H6 Permeability (improved %) | C3H8/CH4 selectivity (improved %) |
|---------------|--------------------------------|----------------------------------|
| Organosilicon | −                              | 7                                |
| polymers      |                                |                                  |
| Various       | 80                             | 56                               |
| polyurethanes |                                |                                  |
| PDMS          | −                              | 22                               |
| PDMSTM        | −                              | 16                               |
| PDMSTMb       | 401                            | 47                               |
| PDMS          | −                              | 12                               |

a Polydimethylsiloxane.
b General formulas −Si(CH3)2CH2−.c General formulas −Si(CH3)2CH2CH2CH2−.

Table 5
The improved percentage for C3H8/CH4 separation through OH-PUU compared to other rubbery membranes.

| Sample        | C2H6 Permeability (improved %) | C3H8/CH4 selectivity (improved %) |
|---------------|--------------------------------|----------------------------------|
| Organosilicon | −                              | −                                |
| polymers      |                                |                                  |
| Various       | 82                             | 72                               |
| polyurethanes |                                |                                  |
| PDMS          | −                              | 51                               |
| PDMSTM        | −                              | 33                               |
| PDMSTM        | 639                            | 116                              |
| PDMS          | −                              | 14                               |

Enhanced phase separation was accompanied by higher gas permeability and selectivity. The increased rubbery behavior of PUU membranes due to improved phase separation explains the more efficient separation of more condensable hydrocarbons through rubbery polymers as the gas transport through a rubbery polymer is dominated by solubility. The aliphatic side chain based PUUs provide a better hydrocarbon separation performance due to the increased affinity of hydrocarbons to the aliphatic side chains. The best results for C3H8/CH4 separation were 186.49 barrer for C3H8 permeability with a 6.51 selectivity by the longest substituted PUU membrane. This performance is comparable with other rubbery membranes which confirms that these polyurethanes are good candidates for this separation.

Author contributions

Afsaneh Fakhar: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Project administration, Resources, Validation, Visualization, Roles/Writing - original draft, Writing - review & editing. Morteza Sadeghi: Conceptualization, Formal analysis, Visualization, Funding acquisition, Project administration, review & editing. Mohammad Dinari: Conceptualization, Formal analysis, Visualization, Project administration, review & editing. Rob Lammertink: Conceptualization, Formal analysis, Funding acquisition, review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jngse.2021.104356.
of polyurethanes. Polymer 45 (5), 1647–1657. https://doi.org/10.1016/j.polymer.2003.12.064.
Tan, H., Xie, X., Li, J., Zhong, Y., Fu, Q., 2004b. Synthesis and surface mobility of segmented polyurethanes with fluorinated side chains attached to hard blocks. Polymer 45 (5), 1495–1502. https://doi.org/10.1016/j.polymer.2003.12.068.
Tan, H., Li, J., Guo, M., Du, R., Xie, X., Zhong, Y., et al., 2005. Phase behavior and hydrogen bonding in biomembrane mimicking polyurethanes with long side chain fluorinated alkyl phosphatidylcholine polar head groups attached to hard block. Polymer 46 (18), 7230–7239. https://doi.org/10.1016/j.polymer.2005.06.032.
Tirouni, I., Sadeghi, M., Pakizeh, M., 2015. Separation of C₃H₈ and C₂H₆ from CH₄ in polyurethane–zeolite 4Å and ZSM-5 mixed matrix membranes. Separ. Purif. Technol. 141, 394–402. https://doi.org/10.1016/j.seppur.2014.12.012.
Toy, L.G., Nagai, K., Freeman, B.D., Pinnau, I., He, Z., Masuda, T., et al., 2000. Pure-gas and vapor permeation and sorption properties of Poly[1-phenyl-2-[p-(trimethylsilyl) phenyl]acetylene] (PTMSDPA). Macromolecules 33 (7), 2516–2524. https://doi.org/10.1021/ma991566e.
Wang, Z.F., Wang, B., Yang, Y.R., Hu, C.P., 2003. Correlations between gas permeation and free-volume hole properties of polyurethane membranes. Eur. Polym. J. 39, 2345–2349. https://doi.org/10.1016/S0014-3057(03)00181-2.
Wang, R., Zhang, Y., Xie, X., Song, Q., Liu, P., Liu, Y., Zhang, X., 2021. Hydrogen-bonded polyamide 6/Zr-MOF mixed matrix membranes for efficient natural gas dehydration. Fuel 285, 119161. https://doi.org/10.1016/j.fuel.2020.119161.
Yampolskii, Y., Pinnau, I., Freeman, B., 2006. Materials Science of Membranes for Gas and Vapor Separation. John Wiley & Sons, Ltd, England, p. 112.
Zhu, H., Jie, X., Wang, L., Kang, G., Liu, D., Cao, Y., 2018. Enhanced gas separation performance of mixed matrix hollow fiber membranes containing post-functionalized S-MIL-53. J Energy Chem 27 (3), 781–790. https://doi.org/10.1016/j.jechem.2017.04.016.
Zhu, W., Qin, Y., Wang, Z., Zhang, J., Guo, R., Li, X., 2019. Incorporating the magnetic alignment of GO composites into Pebax matrix for gas separation. J Energy Chem 31, 1–10. https://doi.org/10.1016/j.jechem.2018.04.013.