Tailoring Crosslinked Polyether Networks for Separation of CO₂ from Light Gases

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Crosslinked poly(ethylene oxide) or poly(ethylene glycol) (PEG) is an ideal membrane material for separation of CO₂ from light gases (e.g., H₂, N₂, O₂, CH₄ etc.). In these membranes, crosslinking is used as a tool to suppress crystallinity of the PEG segments. In spite of the extensive effort to develop crosslinked PEG membranes in the last two decades, it remains a challenge to establish the structure–property relationships. This paper points out the fundamental limitations to correlate the chain topology of a network with the gas permeation mechanism. While a quantitative comparison of the molecular weight between crosslinks of networks and gas permeation mechanism reported by different research groups is challenging, effort is made to draw a qualitative picture. In this review, a focus is also put on the progress of utilization of dangling chain fractions to tailor the gas permeation behavior of PEG networks.

1. Introduction

“A membrane is defined by what it does and not what it is. The membrane restricts the motion of molecules passing across it so that some molecules move more slowly than others or are excluded. A wide range of mechanisms are available for this restriction; for example, size variability of the molecules, affinity for the membrane material, and permeation driving forces typically concentration or pressure difference.” - Richard D. Noble.[1]

The permeation mechanism of gases through nonporous polymeric membranes has been a fascinating research area ever since Graham (1829)[2] and Mitchell (1831)[3] demonstrated the selective permeation of gases through rubbery materials. Graham found a partially filled pig’s bladder expand significantly when it is placed in an environment of carbonic acid gas while in air and water the shape does not change. He speculated that bladders contain capillary channels filled with water through which the water-soluble carbonic acid permeates in and causes the inflation.[2] This notion was dismissed by Mitchell,[3] who discovered a solid piece of gum elastic rubber (obtained from plant origin) is capable of absorbing carbonic acid nearly of its own volume and the permeation of carbonic acid through the gum elastic rubber is related to this phenomenon. A piece of dry bladder also shows similar sorption phenomena, which eliminates the possibility of gas permeation through water-filled capillaries. Further investigation by Mitchell revealed that gases permeate through the gum elastic rubber in the following order (beginning with the fastest)—ammonia, hydrogen sulfide, cyanogen, carbonic acid, nitrous oxide, hydrogen arsenide, olefiant gas, hydrogen, oxygen, carbon oxide, and nitrogen.[3] Graham systematically studied the gas permeation through several membrane materials over a period of 20 years.[4] In 1866 he gave a detailed account of gas permeation through rubbery materials in his paper titled “on the adsorption and dialytic separation of gases by colloid septa.”[5] In this paper, he postulated that the sorption of gases by a rubbery material stems from its chemical affinity towards the gas which is similar to the affinity of solvent and solute in a solution. However, the permeation of the gases through a nonporous material is not representative of sorption only. Gas permeation starts with sorption followed by diffusion of the dissolved gas through the membrane. As a proof of evidence, he showed an increase of temperature tends to increase the gas permeation due to softening of the rubbery materials in spite of the decrease of gas sorption.[5] This paper is regarded as the foundation of the solution-diffusion model, which is the currently accepted gas transport mechanism through nonporous membranes.[6] At present, the solution-diffusion mechanism is the basis to understand the structure–property relationship of polymeric membrane materials at the molecular level. The mathematical statement of the solution-diffusion model is:

\[ P = DS \]  

where \( P \) is the gas permeability, \( D \) is the diffusion coefficient and \( S \) is the solubility coefficient. Permeability is a product of the thermodynamic term, solubility coefficient and the kinetic term, diffusion coefficient. Permeability is the steady-state gas...
flux through a nonporous membrane normalized to the thickness of the membrane under a transmembrane pressure drop. The driving force within the membrane is determined by solubility, which represents the number of gas molecules dissolved in the polymer. Diffusion is the response to the driving force. It represents the mobility of the gas molecules as they diffuse through the membrane. Hence, permeability is an intrinsic property of a gas polymer system which depends upon the number of gas molecules dissolved in the polymer membrane and their rate of migration. There have been parallel developments of experimental methods and theoretical models to determine and understand the gas sorption and the gas diffusion behavior of many polymers. Meanwhile membrane-based gas separation has emerged as a realistic separation technology for large-scale operations. Polymeric membranes are widely used for gas separation owing to their advantage of low cost and ease of fabrication, yet also efficient separation performance. In this paper, we aim to discuss the structure–property relationship on the basis of the solution-diffusion mechanism with a specific focus on crosslinked polyether, especially poly(ethylene glycol) (PEG) based materials. PEG-based membranes are well known for separation of CO2 from light gases (N2, O2, H2, etc.) and hydrocarbons.

2. Global Challenge of CO2 Capture and Crosslinked Polymers for CO2 Separation

The alarming CO2 level in the atmosphere has been the global burning issue for the last few decades. In spite of the tremendous development of the renewable energy sector, the global energy landscape is still dominated by the fossil fuels. According to the bp statistical review of world energy 2020, the global primary energy consumption increased 1.3% in 2019 compared to that of 2018. The fuel shares of the primary energy in 2019 were—33.1% oil, 27% coal, 24.2% gas, 6.4% hydro, 5% other renewable sources excluding hydro and 4.3% nuclear, respectively. While fossil fuels accounted for approximately 84% of the total energy production, in 2020 the CO2 concentration in the atmosphere rose to a record high level of 413 ppm. As the energy industry continues to emit the anthropogenic CO2 development of sustainable CO2 capture technologies is indispensable to mitigate the consequences of global warming and climate change. Separation of CO2 from other gases is one of the major tasks of CO2 capture. Utilization of membrane based gas separation technology for this task has received a lot of attention owing to the inherent attributes, such as energy efficiency, economic feasibility, ease of operation etc. Typically, a thin nonporous layer of a highly selective polymer is coated on a porous support layer of flat sheet or hollow fiber geometry to prepare a composite membrane which is ideal for gas separation. Development of such multilayer composite membranes is in progress to overcome the engineering challenges of gas separation membrane technology. The selective layer dictates the gas separation performance of a multilayer thin film composite membrane while the support layers provide the mechanical strength to the membrane. A large number of polymeric materials have been developed to prepare the selective layer of a thin film composite membrane for the separation of CO2 from industrially relevant gases. Fast and selective transport of CO2 through the polymers to be used for selective layer of the membrane is directly related to the cost and energy demand of the separation process. High CO2 permeation through the membrane leads to a reduction of required membrane area resulting in lower investment costs of the separation plant. Therefore the quest for robust polymeric materials having the combination of high CO2 permeability and desired selectivity over other gases has become the central topic of gas separation membrane research. It is difficult to investigate the structure–property relationships of the materials used as selective layers of the gas separation membranes from the study of a multilayer composite membrane. Hence, researchers are compelled to use free-standing thick films to understand the relationship of the gas permeation mechanism with the chemical structure and morphology of the materials used as a selective layer. The solubility and diffusion of the gases in the polymers are largely dictated by the chemical structure and physical state (i.e., glassy state or rubbery state) of the polymers. Systematic correlations of chemical structure of the polymers and the solution diffusion model of several classes of polymers have been extensively explored such as polymer families, polyolefins, polysiloxanes, polysulfones, polyetherimides, polyethers, polymers of intrinsic microporosity, thermally rearranged polymers etc. The polar–quadrupolar interaction between the ether oxygen of polyethers (especially PEG) and CO2 is widely utilized to prepare CO2 selective membranes through which CO2 permeates faster than light gases. Tremendous progress has been made regarding utilization of PEG based materials for CO2 capture from fossil fuel based power plants and separation of CO2 from hydrocarbon streams for purification of biogas and natural gas. Amorphous PEG is the most widely used polymer for the preparation of such membranes, as it offers a good combination of permeability and selectivity. PEG homopolymers having sufficiently high molecular weight to form a film have also a high degree of crystallinity. This is a disadvantage, as the gas molecules cannot permeate through the crystals. Therefore high molecular weight PEG homopolymers are not suitable for membrane fabrication. Crosslinking reduces the conformational freedom of PEG segments and thus inhibits the packing of PEG segments into crystallites. Therefore the resulting crosslinked membranes have a higher amorphous PEG content and are widely used for CO2 separation. But it is a difficult task to establish a systematic relationship between the gas permeation mechanism and the chain topology of a crosslinked polymer network. The prerequisite to perform such a systematic study is the fabrication of a series of crosslinked thick films with a variation of crosslink density having a narrow average molecular weight distribution between the crosslink junctions. The difficulty originates from the limitation to control the exact network topology during synthesis and the uncertainty associated with the experimental determination of the molecular parameters.

3. Degree of Crosslinking of a Polymer Network

The degree of crosslinking is unequivocally the most important parameter of a network. It can be expressed as the concentration of elastically active chains $v_{el}/v_0$, the crosslink density $\mu_{el}/v_0$, the cycle rank density $\xi/v_0$, and the number averaged molecular weight of the polymer chains between the crosslink junctions, $M_c$ where $v_{el}$ is the number of elastically active chains, $\mu_{el}$ is the
number of crosslinks, $\xi$ is the number of independent circuits in the network (cycle rank) and $V_0$ is the volume of the dry polymer network.$^{[34,35]}$ For an ideal perfect network:

$$\xi = \nu_{c} - \mu_{c} + 1$$ (2)

and

$$\mu_{c} = \left(2/f_{\text{crosslink}}\right) \nu_{c}$$ (3)

where $f_{\text{crosslink}}$ is the number of chains connected to a crosslink junction (crosslink functionality). $M_c$ of a perfect network (i.e., a network without dangling chain ends) can be expressed as

$$\frac{M_c}{V_0} = \frac{\rho}{\nu_{c}V_0} = \frac{2}{f_{\text{crosslink}}} \frac{\rho}{\mu_{c}V_0}$$ (4)

$M_c$, $\nu_{c}V_0$ and $\mu_{c}V_0$ are simultaneously determined by experimental techniques related to macroscopic deformation of a network—swelling, compression, or elongation.$^{[35]}$ The classical statistical molecular models namely, affine model$^{[36,37]}$ and phantom model$^{[48]}$ are normally used to derive the relationships between the molecular parameters and macroscopic deformation of the networks. Both of these models define the structural parameters of an idealized end linked perfect network but describe the spatial fluctuations of the crosslinks differently. The affine network model considers the chain ends of the polymer network are attached to an elastic nonfluctuating background which deforms affinely and the network chains deform in the same manner. The phantom network model considers the chain ends are connected with each other at crosslink junctions which fluctuate around their mean position. The phantom model assumes that the conformations of the network chains depend only on the position of the junction and are independent of the surrounding chains. A brief theoretical background about determination of crosslink density by swelling experiments (Section 4) and stress–strain relationships (Section 5) is provided here in order to help newcomers in the topic to follow the discussion in Sections 6 and 7. An overview of the techniques for the analysis of crosslinked polymers can be found in ref. [39].

4. Swelling of Polymer Networks

A classical method of determination of crosslink density is to empirically monitor the swelling of a real polymer network and to estimate the crosslink density of the real network with respect to a perfect theoretical network. The Flory-Rehner theory of equilibrium swelling$^{[40,41]}$ is often used in this regard. This theory is derived by considering an affine model network which is formed by introduction of occasional tetrafunctional crosslinks between very long polymer chains in the bulk. In this model network, the conformations of the polymer chains are not perturbed due to presence of the crosslink junctions. The polymer chains between the crosslink junctions are free to assume any physical conformation and can be represented by a Gaussian chain distribution. When the polymer network comes into contact with a solvent, it swells and the polymer chains connecting the crosslink junctions are forced to elongate. Consequently, a decrease of the chain conformational entropy and an increase of mixing entropy occur simultaneously due to swelling. When these two counteracting entropies become equal in magnitude the crosslinked network attains the swelling equilibrium.$^{[41]}$ The basis of Flory-Rehner theory of equilibrium swelling is the total free energy involved in the swelling of a neutral (not charged) polymer network ($\Delta F_{\text{total}}$) which is comprised of the free energy gain due to mixing of the pure liquid and the polymer network ($\Delta F_{\text{mix}}$) and the elastic free energy ($\Delta F_{\text{el}}$) penalty which originates from the retractive force of the polymer chains against elongation.$^{[42,43]}$

$$\Delta F_{\text{total}} = \Delta F_{\text{mix}} + \Delta F_{\text{el}}$$ (5)

At the swelling equilibrium $\Delta F_{\text{mix}} = -\Delta F_{\text{el}}$ and the average molecular weight of the polymer chains between two adjacent crosslinks of such a model crosslinked network can be expressed as follows:

$$\frac{1}{M_c} = \frac{2}{M_n} - \left(\frac{\mu_{c}}{\nu_{c}}\right) \left[ \ln \left(1 - \frac{\nu_{2,s}}{\nu_{s}}\right) + \frac{\nu_{2,s}}{\nu_{s}} + \chi_{1} \frac{\nu_{2,s}}{\nu_{s}} \right]$$ (6)

where $M_c$ is the number average molecular weight of the uncrosslinked polymer, $\nu$ is the specific volume of polymer, $V_s$ is the molar volume of swelling solvent, $\chi_1$ is the Flory-Huggins-Staverman interaction parameter between the polymer and the solvent, $\nu_{2,s}$ is the polymer volume fraction at the equilibrium swelling state.$^{[41,43]}$ It is noteworthy that Equation (6) is derived by assuming an isotropic swelling of the model network.$^{[40,41]}$ Bray and Merrill$^{[44]}$ extended Equation (6) for a network where the crosslinks are introduced between polymer chains with a number average molecular weight $M_c$ in a solution of polymer volume fraction $\nu_{2,s}$.

$$\frac{1}{M_c} = \frac{2}{M_n} - \left(\frac{\mu_{c}}{\nu_{c}}\right) \left[ \ln \left(1 - \frac{\nu_{2,s}}{\nu_{s}}\right) + \frac{\nu_{2,s}}{\nu_{s}} + \chi_{1} \frac{\nu_{2,s}}{\nu_{s}} \right]$$ (7)

Equation (7) is an extended form of Flory-Rehner equation (Equation (6)) which considers the network in a relaxed state after crosslinking in solution (before swelling). $\nu_{2,s}$ is the polymer volume fraction at this state. We recover the Flory-Rehner equation by considering $\nu_{2,s} = 1$ in Equation (7), i.e., crosslinking occurred in the bulk state. As mentioned earlier, both Equations (6) and (7) are valid under the assumption that the mean squared end-to-end distance of polymer chains between the crosslink junctions can be represented by a Gaussian distribution. In case of a highly crosslinked system the molecular weight between the crosslinks can be represented by Equation (8) which takes into account the deviation from the Gaussian distribution of the mean squared end-to-end distances of the network chains due to perturbation of the chain conformation by the crosslink junctions.$^{[45,46]}

$$\frac{1}{M_c} = \frac{2}{M_n} - \left(\frac{\mu_{c}}{\nu_{c}}\right) \left[ \ln \left(1 - \frac{\nu_{2,s}}{\nu_{s}}\right) + \frac{\nu_{2,s}}{\nu_{s}} + \chi_{1} \frac{\nu_{2,s}}{\nu_{s}} \right] \left[ 1 - \frac{1}{N} \left(\frac{\nu_{2,s}}{\nu_{s}}\right)^{1/3} \left(\frac{\nu_{2,s}}{\nu_{s}}\right) \right]$$ (8)
where \( N \) represents the number of links per chain between two effective crosslink junctions. For detailed experimental descriptions of determination of \( \overline{M}_c \), the readers are referred to references.\(^{[45,46]}\)

5. Stress–Strain Analysis of Polymer Networks

The stress–strain relationship of a polymer network is also widely used to determine the crosslink density of the polymer network. There are two different approaches to correlate the stress-strain behavior of a polymer network with the molecular parameters.\(^{[37,48]}\) The classical approach is based on deriving a mathematical relation of the stress–strain behavior of an ideal network using a statistical model (e.g., affine network model, phantom network model). The phenomenological method is based on establishing a mathematical framework to solve the stress analysis and strain analysis problem without any molecular or microscopic reference concept.\(^{[49]}\) According to classical rubber elasticity theory of an ideal incompressible polymer network having Gaussian chain distribution, the nominal stress (or engineering stress) in uniaxial extension in the region of low elongation can be expressed as:

\[
\sigma = G \left( \lambda - \frac{1}{\lambda^2} \right)
\]  

(9)

where \( G \) is the elastic modulus, \( \sigma \) is the nominal stress, i.e., force per undeformed cross-section area and \( \lambda \) is the extension ratio.\(^{[50-52]}\) The contribution of chemical crosslinks upon rubber elasticity according to these models can be expressed as:

\[
G_{\text{affine}} = \frac{\nu_0 \beta}{V_0} = \frac{f_{\text{crosslink}}}{V_0} - 2 \frac{\xi RT}{V_0} = \frac{\rho RT}{\overline{M}_c}
\]  

(10)

\[
G_{\text{phantom}} = \left( 1 - \frac{2}{f_{\text{crosslink}}} \right) \frac{\nu_0 \beta}{V_0} = \frac{\xi RT}{V_0}
\]  

(11)

where \( G_{\text{affine}} \) and \( G_{\text{phantom}} \) are the elastic moduli of a perfect ideal network according to affine and phantom network model, respectively.\(^{[53,55]}\) The affine and phantom network models are the two limiting cases of network properties. It is well established that the rubber elastic behavior of a real polymer network is in between the predictions of the affine and phantom network models. The phantom elastic network model is more likely to be valid for a swollen polymer network as the fluctuations of the crosslink junctions are expected to be high in such a state. With the decrease of solvent content the rubber elasticity of the network is expected to shift towards the affine network model.\(^{[54]}\) Several constrained network models, e.g., constrained junction fluctuation model, tube model, or slip tube model have been proposed which take into account the interchain interaction and bridge the properties of two classical unconstrained network models.\(^{[34,55]}\) However, in practice till now the affine network model is widely used to analyze stress–strain behavior of real polymer networks, especially at low deformations. Equations (9) and (10) yield the following relation between \( \overline{M}_c \) and stress–strain behavior.

\[
\sigma = \frac{\rho RT}{\overline{M}_c} \left( \lambda - \frac{1}{\lambda^2} \right)
\]  

(12)

If a plot of engineering stress versus \( \lambda - \frac{1}{\lambda^2} \) is linear, Equation (12) is used to obtain a value of \( \overline{M}_c \). However, Equation (12) does not take into account the deviations originating from Gaussian chain statistics, value of \( f_{\text{crosslink}} \) (trapped) chain entanglements, changes of internal energy with conformational changes, etc. In case of highly crosslinked polymer networks the accuracy of the obtained value of \( \overline{M}_c \) deviates largely from the theoretical \( \overline{M}_c \).

The Mooney-Rivlin equation,\(^{[56-58]}\) a simple phenomenological two parameters equation, is widely used to correlate the crosslink density of the polymer networks with empirical mechanical deformation. The Mooney-Rivlin equation can be written as:

\[
\frac{\sigma}{\lambda - \frac{1}{\lambda^2}} = 2C_1 + 2C_2 \frac{1}{\lambda}
\]

(13)

where \( 2C_1 \) and \( 2C_2 \) are constants. The constant \( 2C_2 \) accounts for the deviation from the deformation behavior of a perfect ideal network. Several factors contribute to the value of \( 2C_2 \), e.g., non-Gaussian chain distribution, chain entanglements, dependence of internal energy on conformations etc.\(^{[59,60]}\) Since Equations (12) and (13) apply only to time independent deformation behavior, it is essential to assume the experimental data is obtained under equilibrium condition and in absence of chemical degradation of the polymer network. Therefore a swelled polymer network is often used for the experiments to attain the equilibrium.\(^{[60]}\) For a swelled polymer network of polymer volume fraction \( \nu_2 \), the Mooney-Rivlin equation can be written as:

\[
\frac{\sigma, \nu_2^{1/3}}{\lambda - \frac{1}{\lambda^2}} = 2C_1 + 2C_2 \frac{1}{\lambda}
\]

(14)

Typically a straight line having an intercept of \( 2C_1 \) and a slope of \( 2C_2 \) is obtained from a plot of \( \frac{\sigma, \nu_2^{1/3}}{\lambda - \frac{1}{\lambda^2}} \) versus \( \frac{1}{\lambda^2} \) and \( \overline{M}_c \) of the polymer network is determined from the following relation.\(^{[59]}\)

\[
\frac{\rho RT}{\overline{M}_c} = 2C_1 + 2C_2
\]

(15)

Although the Mooney-Rivlin equation is widely used to fit experimental data, there does not exist a general agreement regarding the real origin of the constant \( 2C_2 \).

6. Limitations of Statistical Thermodynamic Models and Recent Empirical Advances Using Crosslinked Polyether Networks

In most cases, the statistical thermodynamic models are the cornerstones of our understanding of the macromolecular nature
of crosslinked polymer networks. But the statistical models do not take into account the network defects which are unavoidable in a real polymer network. The formation of a polymer network is a kinetically controlled process. Often a fraction of the polymer chains is attached to the crosslinked network at a single end only (dangling chain fraction) and some unreacted macromolecules are trapped in the network (sol fraction). The statistics of the crosslinking process generates a substantial quantity of elastically ineffective loops where both ends of the chain are connected in the same crosslink junction (loop fraction). Consequently, the macroscopic deformation behavior of a real network deviates from an ideal network to a large extent and the validation of the models using a real network is hampered. The synthesis of defect-free ideal polymer network has been a pursuit of soft matter science for decades. Theoretically, model networks with no dangling chains or in elastic loops can be prepared by complete crosslinking of telechelic polymers with $\alpha,\omega$-difunctional groups using a stoichiometric quantity of multifunctional crosslinker. In such networks, the crosslink points are chemically well defined and the molecular weight of the starting difunctional oligomers is equal to the $M_c$.\(^{[61]}\) In reality, it is not possible to fabricate such ideal networks. But it is possible to minimize the irregularities of the networks by crosslinking the terminal functional groups of monomers or oligomers.\(^{[62]}\) Synthesis of a nearly ideal polymer network formed by cross-end coupling of two tetra-arm PEGs, tetraamine terminated PEG and tetra-N-hydroxysuccinimide-glutarate terminated PEG, (tetra-PEG gel) have been reported.\(^{[63,64]}\) Recently, the validity of the phantom network model to describe the rubber elasticity of a swollen polymer network\(^{[53]}\) and the transition of the elasticity behavior from affine to phantom network model have been demonstrated for the first time\(^{[65]}\) using a tetra-PEG gel. Flory defined the term elastically effective chains, $\nu_{\text{eff}} = 2 \xi$ to take into account imperfections in order to describe the rubber elasticity behavior of a real network. However, due to the limitation to determine $\nu_{\text{eff}}$ experimentally the shear elastic modulus, $G$ of a real network cannot be determined from statistical mechanical theories. Nowadays computer simulations are widely used to explore the fundamental correlations between topology, growth kinetics and elasticity of the real networks.\(^{[66–68]}\) Recently an empirical method to quantitatively determine the primary loops of PEG networks prepared from Diels–Alder chemistry\(^{[69]}\) and click chemistry\(^{[70]}\) has been reported by disassembly of the network into well-defined products followed by spectroscopic analysis. It must be noted that this approach is only applicable for the networks which can be disassembled into well-defined products. For example it is possible to disassemble the $A,B_3$ network presented in Figure 1 by hydrolysis of the ester bonds. A modified phantom network model, called real elastic network theory (RENT), has been derived which takes into account the empirically determined primary loop fractions of the polymer network and shows good agreement with the experimentally determined $G$.\(^{[70]}\)

7. A Qualitative Relation of Molecular Weight Between Crosslinks and Gas Permeation Mechanism of Crosslinked Polyether Membranes

Several well-established crosslinking chemistries have been reported to prepare crosslinked thick films, e.g., epoxyamine curing,\(^{[71–75]}\) urethane chemistry,\(^{[61,62]}\) thiol–ene...
Figure 2. Schematic representation of crosslinked poly(ethylene glycol) diacrylate (PEGDA) network. The effective elastic crosslink density of the network depends on the content of inelastic loops in the network.

click chemistry,[32,76,77] acrylate crosslinking,[45,78–81] sol-gel condensation,[74,82,83] ring opening metathesis polymerization,[84] bisimidazolium mediated crosslinking[85] etc. The functionality and rigidity of the crosslink junction prepared by different chemistries are not comparable. Moreover, the $M_c$ values determined from different techniques (Sections 4 and 5) largely deviate from each other and the theoretical $M_c$. Lin et al.[45] used UV photopolymerization to crosslink poly(ethylene glycol) diacrylate (PEGDA) (Figure 2) of molecular weight 743 g mol$^{-1}$. For the crosslinked PEGDA films (prepared without any diluents) $M_c$ value obtained from Equation (7) was 125 g mol$^{-1}$ and the $M_c$ obtained from Equation (8) was 502 g mol$^{-1}$ while the theoretical $M_c$ was 370 g mol$^{-1}$. They prepared a series of crosslinked PEGDA films having very low sol fractions by varying the concentration of precrosslink solution (aqueous solution of PEGDA and initiator where the amount of initiator was 0.1% of the PEGDA content). A decrease of concentration of the PEGDA content in the precrosslink solution increased the elastically ineffective loop fraction of the crosslinked PEGDA films due to a higher tendency of intramolecular crosslinking. The theoretical crosslinking density and the chemical composition of the resulting networks remained unchanged (82 wt% PEG) but the elastically effective crosslinking density was changed. The permeabilities, solubilities and diffusivities of gases for the series of crosslinked PEGDA were independent of effective elastic crosslink density and/or loop fraction. Kwisnek et al.[76] added 20 mol% of five different multifunctional thiols (Figure 3) of functionality 2 to 4 in PEGDA ($M_n = 700$ g mol$^{-1}$) and crosslinked the mixtures (without any diluent) by UV curing. Compared to the PEGDA network without thiols, the gas permeability through the dithiol containing PEGDA networks was higher while it remained unchanged for the tri- and tetrafunctional containing PEGDA networks. This work implies that the $M_c$ between the crosslink junctions is large enough, the rigidity and the functionality of the tri- and tetrafunctional crosslink joints do not have any influence on gas permeability and selectivity. However, the dithiols decreased the crosslink density and connected some PEGDA segments linearly, i.e., increased the $M_c$ between the crosslinks in some part of the network which led to an increase of gas permeability.

There are other evidences that gas permeability of crosslinked membranes increases with $M_c$ as well. For example, Barrer et al.[86] reported that in highly crosslinked copolymers of tetra(ethylene glycol) dimethacrylate and ethylacrylate having $M_c$ between 350 and 750 g mol$^{-1}$ (obtained from volume compression) the permeability of He, Ne, Ar, Kr, H$_2$, N$_2$, O$_2$, and CO$_2$ increased with the decrease of crosslinking density. Andrady et al.[61,62] crosslinked the terminal hydroxyl groups of poly(propylene glycol) (PPG) having molecular weights in the range of 425–3000 g mol$^{-1}$ with stoichiometric quantities of triisocyanates. An increase of theoretical $M_c$ of the prepared crosslinked network was accompanied with a linear decrease of the glass transition temperature ($T_g$).[62] The increased molecular motion also resulted in a linear increase of H$_2$ and CO permeabilities.[61] Kline et al.[33] investigated the influence of crosslink density and crosslink inhomogeneity of networks having higher than 95% gel fraction prepared via epoxy-amine curing using poly(ethylene glycol) diglycidyl ether with a molecular weight of 500 g mol$^{-1}$ and polyetheramines with molecular weights of 148, 600, 900, and 2000 g mol$^{-1}$, respectively. CO$_2$ permeabilities of the networks gradually increased with decreasing crosslink density.

Kwisnek et al.[32] prepared a series of PEG network membranes using thiol–ene photopolymerization. Mixtures of trimethylolpropanetri(3-mercaptopropionate), 2,2’-(ethylenedioxy)diethanethiol, and tri(ethylene glycol)divinyl ether were crosslinked using 2,2’-dimethoxy-2-(phenylacylophenone as photoinitiator (Figure 4). The crosslink density was controlled by varying the amount of diethiol and trithiol while maintaining a 1:1 thiol:ene ratio. The theoretical
Figure 3. Chemical structure: i) ethylenedioxy diethanethiol ii) ethylene glycol bis(3-mercaptopropionate) iii) trimethylolpropane tri(3-mercaptopropionate) iv) pentaerythritol tetra(3-mercaptopropionate) v) tris[2-(3-mercaptopropanoyloxy)ethyl] isocyanurate. The five different multifunctional thiols used by Kwisnek et al.\cite{76} to investigate the role crosslink joints on gas permeation behavior of the polyether networks.

$M_c$, estimated based on monomer stoichiometry assuming an ideal lattice-like network structure of trifunctional junctions, of the prepared networks were between 467 and 7770 g mol$^{-1}$. The experimental $M_c$, calculated by fitting stress–strain data of tensile test to the affine model (Equation 12) were between 936 and 13100 g mol$^{-1}$. The $T_g$ of the networks scaled linearly against $1/\text{theoretical} M_c$, but two regions of gas permeability as a function of $M_c$ were observed. For a theoretical $M_c$ between 467 and 1040 g mol$^{-1}$ the gas permeability increased with $M_c$ while for higher $M_c$ no change of the gas permeability was observed. This trend of gas permeability was solely dependent on the change of diffusion while the solubility remained constant for the entire span of $M_c$.

For the sake of discussion let us generalize the trend between $M_c$ and gas permeation mechanism observed by Kwisnek et al.\cite{76} for any arbitrary network series where the solubility does not change with crosslinking density. Let us consider two distinct regions as represented in Figure 5. As long as $M_c$ is in region 1 the crosslinking density is high enough to have an impact on the diffusion of gas molecules. Initially, the diffusivity increases sharply with $M_c$ and then levels off slowly. As the diffusion of gas molecules requires the collective motion of only a few repeating units, if $M_c$ is higher than a definite value (i.e., $M_c$ enters region 2 of Figure 5) the collective motion of the repeating units of the polymer segments does not have any further influence on the diffusion of gas molecules. It must be taken into account as $M_c$ increases the polymer chains start to have entanglements. Thus in region 2 for high $M_c$ values the collective motion of the repeating units of the polymer segments are not restricted only by the crosslink junctions but also by entanglements. In fact as the value of $M_c$ becomes substantially higher than the entanglement molecular weight of the polymer segments ($M_e$), there exist several entanglements between two topological crosslink junctions. At this point, the collective motion of the repeating units of the polymer segments are largely dictated by $M_e$ rather than by $M_c$. To the best of our knowledge, there are no reports whether $P$ and $D$ in a chemically crosslinked network are also influenced by $M_e$. In other words, it remains unknown, whether $M_c > M_e$ for the networks having $M_c$ values at the transition point between region 1 and region 2. According to this approximation the $M_c$ of the network series reported by Barrer et al.,\cite{86} Andrady et al.,\cite{61,62} and Kline et al.\cite{33} is in region 1 while that of Lin et al.\cite{45} is in region 2. Several factors prevent a quantitative comparison of the $M_c$ of these network series—chemical nature and flexibility of crosslink joints, flexibility of the chains between the crosslink joints, presence of entanglements, uncertainty associated with different methods of determination of $M_c$, topological defects/difference of the networks etc (as discussed in Sections 4–6). At this point, it is reasonable to raise a question—although Lin et al.\cite{45} showed for a series of crosslinked PEGDA of molecular weight 743 g mol$^{-1}$ that the content of loop fraction does not have any influence on the diffusion of gases, what would be the influence of loop fraction on diffusion of gases if the $M_c$ were lower and the crosslink joints had a lower flexibility? The recent development of empirical techniques for quantification of primary loops by disassembly of the network into well-defined products followed by spectroscopic analysis are particularly propitious to shed light in this regard.

8. Dangling Pendant Group: A Tool to Tailor Gas Permeation

Freeman and co-workers have extensively explored the influence of dangling pendant groups in crosslinked PEG networks to find out the fundamental relationships regarding...
Figure 4. Synthesis of crosslinked network from tri(ethylene glycol)divinyl ether, 2,2’-(ethylenedioxy)diethanethiol and trimethylolpropanetri(3-mercaptopropionate) via photoinitiated thiol–ene click chemistry.

segmental dynamics, fractional free volume (FFV) and gas permeation mechanism. The strategy for preparation of such networks was the copolymerization of PEGDA (molecular weight 743 g mol\(^{-1}\)) or PEGDMA (molecular weight 750 g mol\(^{-1}\)) and a monoacrylate or a monomethacrylate containing different pendant chain end groups, e.g., hydroxyl,[87,88] methoxy,[65,87,88] ethoxy,[88,89] phenoxy,[89] and tris(trimethylsiloxy)silyl[90,91] (Figure 6). To study the influence of pendant group content and functionality on the gas permeation mechanism of the network, it is essential to prevent microphase separation and ensure a homogeneous distribution of the dangling chain fraction all over the network. The underlying features to obtain a homogeneous distribution of the dangling chain fraction are the miscibility and reactivity of the monomers. PEGDA is miscible with several monoacrylates, e.g., 2-ethoxyethyl acrylate (2-EEA), ethylene glycol methyl ether acrylate (EGMEA), 2-hydroxyethyl acrylate (2-HEA), di(ethylene glycol) ethyl ether acrylate (DEGEEA), poly(ethylene glycol) methyl ether acrylate (PEGMEA), poly(ethylene glycol acrylate) (PEG), poly(ethylene glycol) phenyl ether acrylate (PEGPEA), and di(ethylene glycol) phenyl ether acrylate (DEGPEA) (Figure 6). The reactivities of these monomers are very similar, what is essential for the formation of a random copolymer by a radical polymerization. Therefore it is possible to synthesize a homogeneous network by copolymerization of PEGDA and one of these monoacrylates without any diluent. But synthesis of a homogeneous network of PEGDA and 3-[tris-(trimethylsiloxy)silyl]propyl acrylate (TRISA) is only possible in the presence of toluene.[90] Due to the difference in reactivity of the polymerizable acrylate and methacrylate groups of PEGDA and (methacryloxy-hydroxy propoxypropyl)methyl bis(trimethylsiloxyl) silane (SIGMA), respectively, a microphase separation occurs in the PEGDA-co-SIGMA networks. But copolymerization of PEGDMA and SIGMA (Figure 6) results in a visually homogeneous network as both comonomers have the same polymerizable group, i.e., methacrylate.[91] The FFV, subglass transition relaxations, and glass-rubber relaxation of the resulting networks are largely dictated by the length and chemical nature of the terminal group of the dangling chain rather than the crosslinking density.[92,93] A pendant hydroxyl group has a propensity to form hydrogen bonding with other polar groups of the network which hinders the segmental mobility and reduces the FFV of the copolymer network.[93] This interaction has larger impact upon constraining the segmental mobility and reduction of FFV of the network in case of
shorter 2-HEA (one ethylene oxide unit) compared to PEGA (7 ethylene oxide units) (Figure 6). Similarly, the steric hindrance of the bulky phenoxy group has a stronger influence on constraining the segmental motion in case of shorter dangling chains containing PEGDA-co-DEGPEA networks as compared to PEGDA-co-PEGPEA networks. In PEGDA-co-DEGPEA and PEGDA-co-PEGPEA network series both \( T_g \) and FFV increase with the dangling fraction content. Although the TRIS-A contains a bulky tris(trimethylsiloxy)silyl terminal group (Figure 6) the \( T_g \) of the PEGDA-co-TRIS-A networks does not change with increasing dangling chain fraction. But due to the presence of an additional hydroxyl side group in SiGMA the \( T_g \) of the PEGDMA-co-SiGMA networks increase up to 60 wt% SiGMA content. Similar like the phenoxy pendant groups, the bulky tris(trimethylsiloxy)silyl also leads to increase of the FFV of the PEGDA-co-TRIS-A and PEGDMA-co-SiGMA networks irrespective of the change of \( T_g \). The incompatibility of the tris(trimethylsiloxy)silyl group with the PEG segments of the network should also strongly contribute to the FFV of these two copolymer network series. The methoxy and ethoxy pendant terminal groups tend to increase the segmental motion and FFV. The only structural difference between EGMA and 2-EEA (Figure 6) is that the latter contains an ethoxy terminal group instead of methoxy. The bulkier and less polar ethoxy pendant groups lead to a slightly higher FFV and lower \( T_g \) of the PEGDA-co-2-EEA networks compared to the PEGDA-co-EGMEA networks of similar dangling chain fraction. Compared to 2-EEA the DEGEEA (Figure 6) has one more ethylene oxide repeating unit. Even such small difference in the length of the dangling chain fraction leads to lower \( T_g \) of PEGDA-co-DEGEEA networks compared to the PEGDA-co-2-EEA networks. PEGMEA (molecular weight 460 g mol\(^{-1}\)) and PEGA (molecular weight 380 g mol\(^{-1}\)) have approximately 7–8 ethylene oxide repeating units while PEGDA (molecular weight 743 g mol\(^{-1}\)) has 14 ethylene oxide repeating units (Figure 6). Therefore, the amorphous PEG content remains unchanged (approximately 82 wt%) in the PEGDA-co-PEGMEA and PEGDA-co-PEG network series in spite of the change of dangling chain fraction. The relaxation mechanism does not change due to introduction of the dangling chain fraction in the PEGDA-co-PEGMEA and

Figure 5. Schematic representation of the influence of average molecular weight between crosslinks on the gas permeation, \( M_c \), for an arbitrary series of networks where the gas solubility is independent of crosslinking density. The trend is generalized according to the data of Kwisnek et al. for the sake of discussion in this paper.
PEGDA-co-PEGME networks. A more homogeneous relaxation environment (reflected by a narrowing of the glass transition) and less intermolecular cooperativity (reflected by a decrease of the fragility index) occurs in these networks compared to the pure PEGDA network.\(^{93}\) However, the PEGDA-co-PEGMEA and PEGDA-co-PEGMA networks series have completely different segmental mobility and FFV trends due to the presence of methoxy and hydroxyl pendant terminal groups, respectively. An increase of the dangling chain fraction of the PEGDA-co-PEGMA networks leads to a modest decrease of segmental mobility and FFV. On the other hand segmental mobility and FFV increase substantially with dangling chain content in the PEGDA-co-PEGMEA network series.\(^{93}\)

Among the monomers and oligomers of Figure 6, PEGMEA leads to the highest segmental mobility (lowest \(T_g\)) and FFV when copolymerized with PEGDA. \(T_g\) and FFV of the PEGDA-co-PEGMEA series can be correlated with each other by Equation (16).

\[
\text{FFV} = \text{FFV}(T_g) + \alpha \left( T - T_g \right)
\]

where \(\alpha\) is the thermal expansion coefficient of the fractional free volume and FFV(\(T_g\)) is the apparent fractional free volume at \(T_g\). For the PEGDA-co-PEGMEA series \(\alpha = 8.4 \times 10^{-4}\) K\(^{-1}\) and FFV(\(T_g\)) = 0.055.\(^{94}\) Equation (16) implies that the FFV of a polymer increases with the segmental mobility. This direct correlation between segmental mobility and FFV does not apply to all PEGDA based copolymer networks discussed above. As stated before, the FFV increases irrespective to the change of \(T_g\) in the copolymer networks containing phenoxo and tris(trimethylsiloxy)silyl pendant terminal groups. With the exception of the copolymer networks containing phenoxy pendant groups, an increase of permeability is associated with an increase of FFV and vice versa for all the copolymer network series described above. It reveals the change of permeability due to an increase of dangling chain content is largely dictated by diffusion. Freeman and coworkers attempted to quantitatively correlate diffusion coefficient and/or permeability with FFV of the copolymer networks using the Fujita modified Cohen-Turnbull free volume model\(^{95}\) which can be stated as:

\[
D = A_D \exp \left( \frac{B}{\text{FFV}} \right)
\]

where \(A_D\) and \(B\) are temperature independent adjustable constants.\(^{94,96}\) The value of \(B\) depends on the size of the penetrant.\(^{97}\) By combining Equations (1) and (17):

\[
P = SA_D \exp \left( \frac{B}{\text{FFV}} \right) = A_P \exp \left( \frac{B}{\text{FFV}} \right)
\]

where \(A_P\) is a pre-exponential factor which is the product of \(A_n\) and solubility. They have calculated the value of \(A_n\), \(A_P\), and \(B\) for a crosslinked PEGDA network (without any comonomer) by plotting \(1/\text{FFV}\) versus diffusion coefficient and permeability obtained at various fugacities and temperatures.\(^{94,96}\) This set of values of \(A_D\), \(A_P\), and \(B\) fits pretty well to the trend of change of diffusion and permeability with FFV for several copolymer network series described above. Owing to the constant amorphous PEG content, in the PEGDA-co-PEGMEA and PEGDA-co-PEGMA network series \(S\) does not change with dangling chain fraction. The change of permeability occurs merely due to the influence of methoxy and hydroxyl pendant groups on the diffusion of the gases. For these two series, the diffusion coefficient and permeability correlate quite well with FFV when the values \(A_D\), \(A_P\), and \(B\) obtained from crosslinked PEGDA are used in Equations (17) and (18), respectively.\(^{97,93}\) The networks containing short chain alkoxy pendant groups (i.e., PEGDA-co-2-EEA, PEGDA-co-EGMEA, and PEGDA-co-DEGEEA) are also consistent with the model for the values of \(A_D\), \(A_P\), and \(B\) obtained from crosslinked PEGDA, although in these networks the amorphous PEG content decreases with the increase of dangling chain fraction.\(^{88,89}\) The diffusion and permeability of the gases through PEGDA-co-2-HEA networks largely deviate from the model. One possible reason for
the deviation in this case is the difference in free volume elements due to the affinity of the hydroxyl group with polar groups of the network compared to that of the crosslinked PEGDA networks.\[^{88}\] In the PEGDA-co-TRIS-A networks the solubility coefficient of the nonpolar gases increases significantly with the nonpolar tris(trimethylsiloxy)silyl terminal group content. As a result, \(A_P\) is not independent of the chemical composition of the PEGDA-co-TRIS-A networks and the experimentally determined permeability deviates significantly from that predicted by Equation (17).\[^{90}\] Thus, it is not possible to quantitatively correlate the diffusion coefficient and/or permeability with FFV of all the networks discussed above using a single set of values for \(A_D\), \(A_P\), and \(B\).\[^{88-90}\]

Similar like permeability and diffusion, the change of ideal selectivity also depends on the chemical nature of the pendant terminal group. The \(CO_2/CH_4\) and \(CO_2/N_2\) selectivities decrease with increasing dangling chain fraction in both PEGDA-co-EGMEA and PEGDA-co-2-EEA networks. But the decrease is relatively stronger in case of PEGDA-co-2-EEA. In the PEGDA-co-2-HEA series \(CO_2/CH_4\) and \(CO_2/N_2\) selectivity increases with increasing dangling chain fraction. As depicted in Figure 6, the only structural difference between EGMEA, 2-EEA, and 2-HEA are the terminal methoxy, ethoxy, and hydroxyl groups, respectively.\[^{88}\] The higher solubility of the nonpolar gases in the PEGDA-co-TRIS-A and PEGDA-co-SiGMA networks with an increase of tris(trimethylsiloxy)silyl terminal group content leads to lower \(CO_2/CH_4\) and \(CO_2/H_2\) selectivity.\[^{90,91}\] With the exception of PEGDA-co-2-HEA networks, the \(CO_2/CH_4\) selectivity decreases for all the copolymer networks discussed above with the increase of dangling chain fraction, even for the PEGDA-co-PEGMEA networks where the content of amorphous ethylene oxide units does not change with composition. But the \(CO_2/H_2\) selectivity improves in the PEGDA-co-PEGMEA networks. Although the dangling chain fraction leads to an increasing or decreasing trend depending on the chemical nature of the pendant group and the gas pairs, the overall ideal selectivity of all the copolymer networks is dominated by solubility selectivity and the faster permeation of \(CO_2\) as compared to light gases.

9. Summary and Perspectives

The rubbery polyether networks are ideal materials for preparation of membranes through which \(CO_2\) permeates faster than the light gases. The gas molecules diffuse within the rubbery polyether networks through the transient free volumes instantaneously formed due to the dynamics of the polymer segments between crosslink junctions. It is well established for decades that the segmental dynamics of a polymer network is influenced by several topological parameters such as the average molecular weight between the crosslink junctions, stiffness of the crosslink junctions, presence of entanglements, presence of dangling fractions etc. Although the \(CO_2\) selective polyether networks have been extensively reported in literature, the relationships between these topological parameters of the networks and the gas permeation mechanism remains largely unexplored. Often the gas permeation through the networks are reported on the basis of the composition of the casting solution or the ratio of crosslinker and the monomers or oligomers used to prepare the network.

Among the large number of studies on crosslinked polyether networks only few have attempted to empirically determine the topological parameters of the network. The lack of such systematic studies stems from the difficulty to control the chain topology during the synthesis of networks and the fundamental limitations of experimental determinations of the parameters related to the chain topology of the networks. The limiting factor of the experimental determination of the network parameters based on the theories of rubber elasticity and some recent advances in this regard are pointed out in this paper. While there are some attempts to correlate the gas permeation mechanism with empirically determined crosslink density, the influence of entanglements has not been discussed before. The permeability and diffusivity of the gases in crosslinked polyether membranes change only at high crosslink density while at lower crosslink density they remain unchanged. It is likely that entanglements play the dominant role for restriction of segmental motion (i.e., formation of the transient free volumes) when the crosslink density is low. However, up to now there is only little experimental evidence to support this statement. While the dangling chain fractions are topological defects of an ideal network, the group of Benny Freeman has successfully implemented the dangling chains as a tool to tailor the segmental dynamics and FFV of the polyether networks. Both the length and the terminal functional group of dangling chains were utilized to tune the permeation of gases through the polyether networks. However, besides crosslink density and dangling chains there are more parameters which can be studied. Here we mention some parameters and refer only to studies on polybutadiene melts and networks carried out by the group of Reimund Stadler a few decades ago, which were not related to membranes for gas separation, but may stimulate further systematic investigations in this direction also using other polymers. Free oligomers in a polymer network have been reported to show nematic coupling interactions (also called orientational or segmental correlation) which depend on their molecular weight.\[^{98}\] Besides such semi-interpenetrating polymer networks (semi IPNs) of similar chemical species, also full IPNs of two similar networks could be interesting, especially for the networks having high crosslinking density. Moreover, thermally reversible crosslinks may be an additional possibility to influence the permeation behavior.\[^{99}\] Furthermore, thermally reversible crosslinks can be combined with permanent crosslinks in the same network.\[^{88}\] Besides networks of one component, also multicomponent networks with similar topologies can be built, which may lead to new membranes with tailored permeation properties.\[^{100}\] These are only some examples of many possibilities to vary polymer network composition, functionality, and topology, which have not been investigated so far.

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Conflict of Interest

The authors declare no conflict of interest.
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