Water Swelling Behavior of Poly(ethylene glycol)-Based Polyurethane Networks

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ABSTRACT: Defects in a polymer network complicate an accurate calculation of structural parameters such as the molar mass between cross-links $M_c$, typically obtained from experimental swelling data. In this paper the formation and structure of poly(ethylene glycol) (PEG)-based polyurethane networks containing PEG-mono methyl ether dangling chains are studied. The phantom network model can describe the swelling behavior of these networks only when a composition-dependent interaction parameter is used and the formation of allophanates is accounted for. A clear transition in the network formation is found at the PEG network precursor molar mass at which entanglements are formed in the melt. Correction factors based on structure calculations using the Miller–Macosko–Vallé probability approach are proposed and validated for an accurate calculation of the $M_c$ of these defect-containing networks. This provides a new approach for studies that requires an accurate estimate of the $M_c$ only based on experimentally straightforward swelling experiments.

INTRODUCTION

Cross-linked polymer networks have a widespread use in numerous technical applications of great importance for our daily life, ranging from rubber tires6,15 to drug release carriers3,4 and functional coatings5,6 among others. The final network properties and morphology depend mainly on the network architecture but also on the chemical nature of the polymer material. For instance, the solvation properties of polymers are utilized for the design of cross-linked networks which swell in the presence of a solvent. A good example of this are hydrogels, which rely on the capacity to absorb a substantial amount of water for the application they are designed for.3,4,7,8 Although (swollen) polymer networks have been studied for almost a century, a universal and complete theoretical understanding (swollen) polymer networks have been studied for almost a century, a universal and complete theoretical understanding of their structure–property relation is still lacking.9,10 This understanding is severely complicated by the fact that network defects are unavoidably present in all real polymer networks. Such defects are diﬃcult (if not impossible) to detect directly by an experimental approach, and their theoretical description is rather challenging.

The network architecture and structure parameters of a polymer network are of great importance for material (bulk) properties as the network moduli7,10 and drug-release rate3,4 as well as surface properties, e.g., antifouling,15–17 self-cleaning,18 and lubricity14–16. To accurately describe defect-containing networks, the main aim of this study is to use straightforward but accurate experiments and theoretical considerations to determine the structure–property relation of chemically cross-linked swollen polymer networks. Particular attention is dedicated to an accurate calculation of the molecular mass between cross-links $M_c$ from swelling experiments when the network contains dangling network chains, which can be seen as network defects.

Given the high importance of polyurethanes (PUs) in general,1,17 and their potential use as hydrophilic networks in the biomedical field in particular, this study focuses on hydrophilic PU-networks. Because a well-defined network architecture is required, the use of an end-linking step growth polymerization chemistry is preferred over free radical initiated chain growth polymerization chemistries.18,19 Poly(ethylene glycol) (PEG) is a hydrophilic polymer and is widely accepted in the biomedical field for its biocompatibility and antiprotein fouling properties.16,20 Both PEG and PEG monomethyl ether (mPEG) are easily available in a range of well-defined molecular masses with low dispersity. Therefore, hydrophilic PU networks, built of PEG, mPEG, and a tri-isocyanate cross-linker unit, were selected as model networks (see Figure 1).

In this study the preparation of PEG-based PU networks containing dangling mPEG network chains based on various PEG-diols, as well as mPEG concentrations and chain lengths, is described. The effect of the network precursor and dangling chain mass on the swelling properties of the formed networks was investigated experimentally. From a theoretical point of
The functionality of the network junctions, during the network formation (which is unity when the molar volume of the solvent, \( \rho_s \), is given by (see SI-I, eq SI-7 = eq 1)

\[
M_c = \frac{\rho_n V_{\Phi n_0}^{-1/3}}{\ln(1 - q_n) + q_n + \chi q_n^2}
\]

Here \( \rho_n \) is the density of the dry (nonswollen) network, \( V \) the molar volume of the solvent, \( \chi \) the polymer-solvent interaction parameter.

The other model often used is the James–Guth phantom network model, for which it is shown that it describes best the mechanical properties of the network. A more recent approach incorporated topological “loop” defects of various order in the classical phantom and affine network theories of elasticity. The results led to the so-called real elastic network theory (RENT) that describes how loop defects affect bulk elasticity, still in an approximate way. Hence, although both experimental and theoretical works have provided a better understanding of the influence of network imperfections on network swelling, theoretical descriptions of their effect on the network swelling are still largely absent. The only exception is a correction for dangling chain ends by Flory in which the number of network chains is corrected to the number of elastically effective network chain elements \( V = (1 - (2M_c/M_n)) \) and using \( V = V/(\rho_n^{-1}M_c) \), where \( M_n \) is the molar mass of polymer network chains before cross-linking and \( V \) the volume of the network. This correction is originally proposed for randomly cross-linked rubbers via vulcanization processes, in which tetrafunctional cross-links are formed by randomly joining two long chains. Such a process inevitably leaves dangling chain ends in the network structure once no further reaction occurs further along the chain. From a fundamental point of view this correction is also suitable for random networks cross-linked by radiation and is often used for hydrogel type networks in the biomedical field. The correction is also applied for networks prepared from end-linking chemistries. However, given the nature of the correction, its use for networks prepared from end-linking chemistries seems questionable.

Next to the expression for the dangling chains given by Flory, it should be noted that a great deal of work is done describing the effect of trapped chain entanglements inside the network. Half a century ago, Langley introduced an expression for the so-called trapped entanglement factor \( T_c \) based on a probability approach, after which it became apparent that trapped entanglements significantly contribute to the elastic properties of polymer networks. It is recognized that moduli from stress–strain experiments as well as the free energy terms from network models have to be properly corrected for the effect of entanglements. Although additional factors to take entanglements into account are
added to models, a comprehensive analytical description is absent.9,10,35
An interesting approach capable of estimating the effect of loops upon the shear modulus quantitatively is given by Zhong et al.93 and Lang.94,95 These authors showed that by quantifying the number of primary loops, the number of secondary and higher loops is fully fixed and that their effect can be fully incorporated in the description of network elasticity by using the concept of an effective phantom chain.

§ MATERIALS AND METHODS

Materials. Poly(ethylene glycol) (PEG) with different molar masses (M = 1000, 2000, 4000, 6000, 10000, and 20000 g mol⁻¹) and poly(ethylene glycol) monomethyl ether (mPEG) with different masses (M = 750, 2000, and 5000 g mol⁻¹) were employed. Sigma-Aldrich, all disparities D = M/Mc < 1.06 (SEC) were dried for 14 h at 40 °C at 20 mbar before use. Further purification of PEG via azotropic distillation did not significantly improve the purity of the compounds, as shown by NMR. Trimerized hexamethylene diisocyanate (HDI) (equivalent functional weight of 183 g mol⁻¹) was kindly provided by Perstorp as tolonate HDT-LV2 and used as received. Cyclohexanone (99.8%, Sigma-Aldrich) was dried on molecular sieves before use.

Preparation of Polyurethane PEG-Diol-Based Networks. All glassware was dried in an oven at 100 °C at least 14 h prior to use. Network precursor stock solutions (typically 10 mL) of PEG (10–50 wt %) and of tHDI (50 wt %) were made by dissolving PEG and tHDI in cyclohexanone at 55 °C and room temperature, respectively. This was done in closed glass vials under an argon blanket and continuous stirring. Contact of oxygen with the network precursors was minimized as much as possible to prevent possible degradation of the polymers during network preparation. Therefore, every time a vial was opened during the whole preparation procedure, the glass was thoroughly flushed with argon after opening and before closure. Moreover, the lid was wrapped with Paraffin tape after closure.

Network formulation solutions (typically 10 mL) were prepared by mixing different ratios of precursor stock solutions in a closed glass vial at 55 °C under an argon blanket. The NCO/OH molar ratio of each formulation was kept at 1.1 to ensure full conversion of the OH groups and to compensate for possible side reactions. The formulation solutions were poured in precleaned and dried flat bottom aluminum foil molds with a diameter of 60 mm and put on a formulation solutions were poured in precleaned and dried groups and to compensate for possible side reactions. The each formulation was kept at 1.1 to ensure full conversion of the OH

Experimental Network Formation Characterization. FTIR absorbance spectra of cured networks were recorded in attenuated total reflection (ATR) mode by using a Varian Excalibur FTIR-3100 equipped with a diamond Specac Golden Gate ATR setup. Measurements were performed over a spectral range of 4000 to 650 cm⁻¹ with a resolution of 2 cm⁻¹. For each measurement 50 spectra were averaged. Next to recording the spectra of cured networks, the curing reaction at different temperatures of a PUPEG2000 network was followed in time on the ATR stage, equipped with an Eurotherm 2416 temperature controller. Approximately 10 mL of the network formulations was loaded on the ATR crystal, after which spectra were recorded every 30 s for a duration of 2 h under a continuous argon flow. For each measurement 12 spectra were averaged. Given the large overlap of the C=O urethane stretch vibration (1720 cm⁻¹) and the isocyanurate C=O stretch vibration (1675 cm⁻¹) present in the networks, and moreover the C–N urethane stretch vibration band (1550 cm⁻¹) being located at the fingerprint region, a reliable quantitative analysis of NCO to urethane conversion from the IR absorbance spectra is impracticable. Therefore, only the disappearance of the N==C=O asymmetric stretch vibration at 2270 cm⁻¹ was used to analyze the NCO conversion of the cured networks at the surface. The normalization of the peak area was done by dividing its area by the peak area of the isocyanurate core vibration (766 cm⁻¹) and subsequently with this ratio between both peaks at t = 0 min.

The dry weight of the networks directly after curing and after extraction was measured gravimetrically. The amount of extractable material L gives a qualitative indication of the network formation and is calculated via L = ((m₁−m₀)/m₀) × 100%, where m₁ and m₀ are the initial weight of a network after curing and of the extracted dry network, respectively. The extracted networks were immersed in demineralized water again to swell to equilibrium for at least 14 h. The swollen weight of the networks msw was measured gravimetrically directly after the networks were taken out of the water and after gentle removal of all excess water with absorbing lint free paper. Based on the absolute water uptake, the total polymer network volume fraction ϕn in the swollen network is calculated via

\[ \phi_n = \frac{V - V_d}{V} = \frac{1}{Q} \]

where V is the total volume of the swollen network, Vₚ is the volume of polymer network in the total swollen network, Vₑ is the initial volume of the network before swelling, and Q is the volumetric equilibrium swelling ratio. Because the network is cross-linked in the absence of solvent (i.e., during the second step in the curing procedure), Vₑ = Vₑ. The swelling ratio Q can be calculated from the measured water uptake via

\[ Q = \frac{V}{V_d} = 1 + \frac{\rho_e}{\rho_{H_2O}} \left( \frac{m}{m_0} - 1 \right) \]

where \( \rho_{H_2O} \) is the density of water (1 g cm⁻³) and \( \rho_e \) the density of the nonswollen network. Values for \( \rho_e \) slightly differ for different network formulations, given the different overall network composition. Therefore, \( \rho_e \) of each different dry network is estimated via

\[ \rho_e = \rho_{PEG(E)} + \rho_{H_2O} \left(1 - \phi_{EG} \right) \]

assuming no excess volume upon mixing and polymerization, where \( \rho_{PEG(E)} \) and \( \rho_{H_2O} \) are the densities of the PEG network precursors and HDI in the network, respectively. Both are calculated with Molecular Modeling Pro software® using the molar volumes. \( \phi_{EG} \) is the volume fraction of ethylene glycol (EG) units in the dry network and is calculated from the mass ratio of the network precursors via their densities by

\[ \frac{1}{\phi_{EG}} = 1 + \frac{\rho_{PEG}}{\rho_{H_2O}} \left( \frac{1}{\phi_{EG}} - 1 \right) \]

where \( \phi_{EG} \) is the initial weight fraction of EG units in the dry network. Finally, we note that preliminary attempts to characterize the films by mechanical measurement failed due to the extreme fragility of the films.
**RESULTS AND DISCUSSION**

**Network Formation.** It is critical to use a network preparation procedure that ensures proper network formation without leading to ambiguities in the structure analysis. This requires, first, the use of (nearly) monodisperse raw materials. Here raw materials with $D = M_n/M_w < 1.06$ were used for all components, so that in this study effects of polydispersity are minimal. As a second requirement, the degree of conversion should be (very near) unity. Therefore, the NCO conversion was followed in time, and the amount of extractable material after cross-linking was determined. Both led to the conclusion that (nearly) full conversion was reached. Hence, in this study fully cross-linked, monodisperse networks are employed.

After optimization, the two-step procedure, as described in the Materials and Methods section, was used for the preparation of the PUPEG2000 networks. The absence of the NCO asymmetric stretch vibration at 2270 cm$^{-1}$ after cross-linking for 120 min at 125 °C in N$_2$ indicates a complete conversion of the NCO groups near the surface, while the increasing absorbance band at 1550 cm$^{-1}$ shows the formation of urethane groups. Moreover, these films showed no curling during or after preparation was observed. No side reactions were observed, and the use of a N$_2$ atmosphere prevented the influence of water. Finally, hardly any extractable material was detected for these networks (Table 1). For a detailed analysis, see Supporting Information SI-II. An overview of the volumetric swelling ratio $Q$ of PUPEG2000 networks prepared with varying film thicknesses (measured with a digital caliper with an accuracy of $\pm 1 \mu m$) and cast from network formulations with varying solid weight contents is also given in SI-II. No trends can be observed between the solid weight content of the network formulation, resulting film thickness, and volumetric swelling ratios of the networks, which indicates no influence of the film thickness on the swelling ratio of the networks prepared in this thickness range via the preparation procedure used.

Finally, it might be argued that the tHDI cross-linker, being a relatively hydrophobic molecule, associates in the (much) more hydrophilic environment of the coating components. In fact, this should than occur for all NCO ratios used. However, the amount of allophanates formed is proportional to the excess NCO, and no allophanates are observed for NCO:OH $= 1.0$ (as demonstrated by NMR, see SI-III). Furthermore, a close proximity of tHDI molecules is a prerequisite for allophanate formation (see SI-III). Finally, cross-linking is done at 125 °C so that association is typically small. Hence, we infer that any significant tHDI association during curing is highly unlikely.

### Table 1. Experimentally Measured Amount of Extractable Material $L$ and Mass Ratio $m_{eg}/m_0$ and Theoretically Calculated Ethylene Glycol Fraction in Dry Network $\varphi_{EG}$, Dry Network Density $\rho$, and Polymer-Water Interaction Parameter $\chi$ Used to Calculate the Volumetric Swelling Ratio $Q$ and the Polymer Fraction in Swollen Network $\varphi_P$ of the Prepared PUPEG-Based Networks without MPEG Dangling Chains

| PUPEG | $L$ [%] | $m_{eg}/m_0$ [g/g] | $\varphi_{EG}$ | $\rho$ [g cm$^{-3}$] | $Q$ [V/V$^0$] | $\varphi_P$ | $\chi$ |
|-------|--------|---------------------|---------------|----------------------|-------------|-----------|------|
| PEG1000 | <0.1 | 2.22 ± 0.09 | 0.712 | 1.238 | 2.50 ± 0.11 | 0.400 ± 0.016 | 0.628 ± 0.008 |
| PEG2000 | <0.1 | 3.01 ± 0.17 | 0.835 | 1.222 | 3.45 ± 0.20 | 0.291 ± 0.017 | 0.582 ± 0.007 |
| PEG4000 | <0.1 | 3.81 ± 0.08 | 0.908 | 1.214 | 4.40 ± 0.10 | 0.227 ± 0.005 | 0.555 ± 0.002 |
| PEG6000 | <0.1 | 4.24 ± 0.19 | 0.937 | 1.210 | 4.92 ± 0.23 | 0.204 ± 0.009 | 0.546 ± 0.004 |
| PEG10000 | <0.1 | 4.58 ± 0.04 | 0.961 | 1.207 | 5.32 ± 0.05 | 0.188 ± 0.002 | 0.539 ± 0.001 |
| PEG20000 | <0.1 | 5.09 ± 0.12 | 0.980 | 1.205 | 5.93 ± 0.14 | 0.169 ± 0.004 | 0.531 ± 0.002 |

*Dry film thickness of all networks ± 120 μm. The error shows the mean absolute deviation from the mean value.*
125 °C for 1 h) resulting in $T_g$ on the order of ~40 °C, allophanate formation78–80 (reaction of an NCO group from a tHDI molecule with the N–H group of a urethane connected to another tHDI entity; see SI-III) has taken place, as proven by swollen state $^{13}$C NMR. The formation of such allophanates gives rise to effectively five-functional cross-linking junctions, which, apart from the overall decrease of network junctions upon combination of junctions, will influence the swelling properties of the networks and needs to be taken into account when calculating the $M_c$. For the stoichiometric imbalance $\text{NCO}:\text{OH} = 1.1$, a small fraction of allophanates are formed. Moreover, for a ratio $\text{NCO}:\text{OH} = 1.0$, no allophanates are detected, while for a ratio 1.2 about twice the amount is observed as for 1.1 (see SI-III). Therefore, the excess of initial NCO groups is consumed via the formation of allophanates once no available OH groups are present anymore. Hence, 6 out of 11 three-functional tHDI molecules will combine into 3 five-functional network junctions (3 out of 33 NCO groups react with an already formed urethane given that $\text{NCO}:\text{OH} = 1.1$). From the initial 11 three-functional network junctions, 5 three-functional junctions still remain. Therefore, the overall network junction functionality $f$ will become $(5 \cdot 3 + 3 \cdot 5)/8 = 3.75$, taking allophanate formation into account. As the amount of allophanate scales with the excess tHDI, $f = 3.75$ is used throughout. For further details, we refer to SI-III.

Network Swelling. As stated in the Introduction, the swelling behavior of the networks is expected to be best described by the phantom model. Furthermore, since the affine and phantom models are in fact the two limits of the more sophisticated Flory–Erman constrained junction model (see SI-1), the behavior of real swollen networks should indisputably lay between these limits. Calculated values for $M_c$ from the measured swelling ratio for both the affine (eq 1) and phantom model (eq 2) for a 3-functional cross-linker, as well as the corrected phantom model taking into account the formation of allophanate by using $f = 3.75$, are given in Table 2 and shown in Figure 3a. All values used for the network parameters are given in Table 1, whereas the molar volume of water is taken as $V_w = 18.07 \text{ cm}^3$. Figure 3 shows that two scaling regimes (for networks prepared with “high” and “low” $M_c$ precursors) can be identified, regardless of the model used.

**Table 2. Calculated Mean Mass between Cross-Links $M_c$ of PEG-Diol-Based PU Networks Using the Affine Model (Eq 1), Phantom Model, and Phantom Model Corrected for Allophanate Formation (Eq 2)**

| PUPEG        | mean $M_c$ [g mol$^{-1}$] |
|--------------|---------------------------|
|              | affine standard, $f = 3$ | phantom standard, $f = 3$ | phantom corrected, $f = 3.75$ |
| PEG1000      | 1335 ± 213               | 342 ± 83                   | 752 ± 119                   |
| PEG2000      | 3552 ± 562               | 1385 ± 210                 | 1923 ± 308                  |
| PEG4000      | 6335 ± 318               | 2410 ± 116                 | 3375 ± 162                  |
| PEG6000      | 7983 ± 752               | 3007 ± 271                 | 4115 ± 306                  |
| PEG10000     | 9298 ± 174               | 3480 ± 62                  | 4810 ± 137                  |
| PEG20000     | 11392 ± 509              | 4227 ± 181                 | 5815 ± 164                  |

The error shows the mean absolute deviation from the mean value.

First, we focus on the low-$M_n$ regime to elucidate on the validity of the different networks models, whereas in the next section the focus is put on a more detailed evaluation of the phantom model in which $f = 3.75$ is used. For networks prepared with low-$M_n$ precursors (up to 4000 g mol$^{-1}$), the value for $M_c$ calculated by using the affine model gives masses between cross-links on the order of 1.5 times higher than the $M_c$ of the precursor used, while the phantom model yields masses on the order of 0.6 times the $M_c$ of the precursors used. Assuming that the effect of trapped chain entanglements only plays a role in networks prepared from high-$M_n$ precursors (see the next section), one expects a near one-to-one scaling of $M_c$ with $M_n$ for networks prepared with low-$M_n$ precursors. The affine model yields a significantly higher $M_c$, which would indicate the formation of a loose network structure with a high fraction of network imperfections and unreacted precursors. Given the absence of extractable material after network formation (see Table 1), this scenario is highly contradicting, thereby confirming that this model is not describing the swollen networks properly.

On the other hand, the standard phantom model with $f = 3$ yields a $M_c$ almost 2-fold lower than $M_n$. However, when an overall cross-link functionality of 3.75 is used in the phantom model, the slope of $M_c$ vs $M_n$ is near unity for the low-$M_n$ precursors, as can be seen from Figure 3. This validates this corrected phantom model which takes the formation of allophanates into account. Next to the sensitivity of the model to the correct junction functionality, the model is extremely sensitive to the value for the polymer–water interaction parameter $\chi$ (see SI-IV). The chosen network polymer volume fraction dependent value for $\chi$ (eq 6), based on existing experimental data,77 seems to be an accurate choice for describing these networks.

Network Swelling: The Effect of Trapped Physical Entanglements Using Precursors with $M_n > M_c$. A more detailed evaluation of the calculated $M_c$ using the phantom model for which the junction functionality is corrected for allophanate formation is shown in Figure 3b. A clear transition of the slope of the curve is visible between networks produced with precursors with a $M_n$ of 4000 and 6000 g mol$^{-1}$. Fitting the values of $M_c$ of the networks prepared with $M_n < 4000$ g mol$^{-1}$ to a weighted linear fit through the origin (Adj $R^2 = 0.993$) and the values of $M_c$ of the networks prepared with $M_n \geq 6000$ g mol$^{-1}$ to a weighted linear fit (Adj $R^2 = 0.998$) gives an intersect of both fits at a network precursor $M_n$ of about 4500 g mol$^{-1}$. The slopes of both fits can be associated with all network junction constraints and network imperfections not
accounted for in the theoretical network model. The transition from the first linear regime for \( M_c \) (for \( M_n < 4500 \text{ g mol}^{-1} \)) to the second linear regime with a lower slope (for \( M_n > 4500 \text{ g mol}^{-1} \)) can be seen as a transition between networks formed, both having a constant amount of topological constraints but with additional constraints for the second regime (more constraints \( \rightarrow \) less network swelling \( \rightarrow \) lower slope). From a molecular model point of view this can be interpreted as the additional contribution of trapped physical entanglements to the network modulus.\(^{60-65}\) The \( M_n \) corresponding to the intersect (\( \approx 4500 \text{ g mol}^{-1} \)) is apparently the molar mass of the network precursor above which trapped physical entanglements start to contribute to the network topology. This intersect value is close to the experimentally measured critical molar mass for PEG to form physical entanglements in the melt \( M_c \) (4410 g mol\(^{-1}\) for linear PEG)\(^{55}\) as well as the calculated critical molar mass with the entanglement model proposed by Wool (4500 g mol\(^{-1}\)).\(^{55}\) We conclude that near ideal networks are formed for PEG-diol-based PU networks using PEG with a \( M_n \) below \( M_c \) (given the slope of the fit 0.88), with a transition to PEG-diol-based PU networks which contain additional physical entanglements above this threshold.

Although it is known that trapped entanglements play an important role in the overall network properties, these studies often focused on randomly cross-linked networks and highly swollen gels with precursors (far above) \( M_c \) or ideal well-defined PDMS networks.\(^{49,59,60,82-84}\) Less attention was given to describing the structure parameters based on swelling experiments as demonstrated here is, to the best knowledge of the authors, not reported in the literature so far for water swollen PEG-based PU networks.

**PEG-Based PU Networks with MPEG Dangling Network Chains.** Various PEG-based PU networks containing mPEG (\( M_n = 750, 2000, \) and \( 5000 \text{ g mol}^{-1} \)) were prepared to study the effect of the insertion of network dangling chains on the volumetric swelling ratio \( Q \) and the mass between cross-links \( M_c \). These networks did not show either any NCO groups left after curing or the tendency to curl. Only the PUPEG1000mPEG5000 networks broke into smaller pieces during swelling and delamination of the mold, most likely due to too high swelling induced stresses in the network.

**Proposed Corrections for the Calculation of \( M_c \) of PU Networks Containing Dangling Chains Defect.** As stated before, except for the adjustments for randomly cross-linked linear long chains by Flory,\(^{24}\) classical network models assume ideal network structure relations to calculate the mass between cross-links and/or network moduli. As shown by Saalwächter and co-workers\(^{59,87}\) by \(^1\)H double quantum low field NMR (DQ_NMR) studies on PDMS networks, it is important to correct the phantom network model for the fraction of elastically active material in the network. For an estimate of the molar mass between cross-links \( M_c \), they directly multiplied the numerator of eq 2 with the actual fraction of elastic active material as measured in their DQ NMR experiments.

Instead of proposing one single correction factor from experimental NMR data, we propose to use correction factors based on network structural arguments. A short dangling network chain is elastically inactive. Moreover, the moment a cross-linking point which is bearing a dangling chain has less than 3 connections to the “infinite” network, it is not an effective junction in the network anymore. Therefore, the presence of dangling chains in a network changes both \( \nu \) and \( \mu \) in the network structure relations (eq SI-3 to eq SI-5). Instead of using the ideal numbers for \( \nu \) and \( \mu \), it would be more appropriate to correct both parameters for the effective amount of elastically active chains \( \nu_{\text{eff}} \) and network junctions \( \mu_{\text{eff}} \) via a simple correction factor.
 following corrected phantom model for the calculation of network precursors. Therefore, by use of this approach, it is assumed that the experimental average final network structure can be related to the ideal theoretical average network structure at the calculated extent of the reaction based on the amount of measured soluble material.

If soluble material is detected after extraction, not all initial network precursors will end up being part of the network (i.e., soluble material will be washed away). Therefore, small corrections need to be applied to calculate the real effective fractions of the resulting extracted network (since this network will be the dry network which will be swollen during the swelling experiments). The fraction of elastically active material in the extracted network \( \alpha \) is calculated by dividing \( W_e \) obtained from the MMV calculation, by the fraction of material ending eventually ending up in the extracted network via

\[
\alpha = \frac{W_e}{1 - W_e}
\]  

The same is true for the effective amount of elastically active network junctions in the network \( \beta \). To take the aliphane formation into account, the system is corrected assuming that the initial 10% excess NCO leads to an instantaneous prereaction yielding a fraction of A\(_c\) precursors before the cross-linking starts while the overall stoichiometric imbalance \( r \) is corrected to 1. The prereaction of 3 out of 33 NCO groups yields 3 5-functional cross-linkers while 5 3-functional cross-linkers remain (see SI-III). This results in a weight fraction of 5/11 for A\(_c\) and 6/11 for A\(_s\) of the initial cross-linker content.

A cross-linker molecule A\(_c\) or A\(_s\) will end up being an effective junction as long as it is connected with at least three ends to the infinite network structure. In other words, any cross-linker molecule that is connected with only two ends to the infinite network is still contributing to the weight fraction of elastically active material but is not an effective network junction anymore. Therefore, the actual mass between cross-links increases since the total mass of the elastic active components now is “shared” between less active cross-linking points. When the cross-linker molecule is only connected with one end to the infinite structure, it is neither elastically active nor an effective network junction. Therefore, the fractions of active cross-linker molecules \( f_{A_c} \) and \( f_{A_s} \) are given by

\[
f_{A_c} = \sum_{i=1}^{k} \left[ \left( \sum_{j=1}^{n_f} P(F_{A_c}^{j})^{j-i} (1 - P(F_{A_c}^{j}))^{j-i} \right) \right]
\]

and

\[
f_{A_s} = \sum_{i=3}^{k} \left[ \left( \sum_{j=1}^{n_f} P(F_{A_s}^{j})^{j-i} (1 - P(F_{A_s}^{j}))^{j-i} \right) \right]
\]

From these fractions, \( \beta \) is given by dividing the absolute weight fraction of active cross-linker molecules by those actually ending up in the network via

\[
\beta = \frac{f_{A_c} C_j + f_{A_s} C_j (1 - C_j)}{1 - (f_{A_c} C_j + f_{A_s} C_j (1 - C_j))}
\]  

where \( C_j = [A_j]/([A_c] + [A_s]) \) is the ratio of the A-bearing precursors and \( f_{A_c} \) and \( f_{A_s} \) are the fractions of the cross-linker molecules ending up as soluble material.

Water Uptake and Amount of Extractable Material. An overview of the measured amount of extractable material \( L \), volumetric swelling ratio \( Q \), and PEG weight fraction \( \varphi_{PEG} \) of all
prepared PEG-mPEG based PU networks (all prepared in 2-fold) is given Table 3. The table also contains the theoretical values of extractable material as given by the calculated weight fraction of soluble material at the extent of the reaction for \( p = 1 \) for an \( A_3A_5B_2B_1 \) system, calculated by using the MMV probability approach. More details on the input parameters for the calculations are given in the next section. It can be seen from Table 3 that the networks prepared with mPEG precursors show a measurable fraction of extractable material, in contrast to the mPEG free networks discussed previously. Moreover, the measured amount of extractable material is larger as expected from the calculated soluble fraction for ideal networks. This discrepancy indicates the presence of additional network defects since more material ends up in the soluble fraction after the network formation. A reason for this can be the fact that the probability approach does not consider topological restrictions on the functional groups (i.e., the physical possibility to meet each other at higher conversions).

### Table 3. Amount of Experimentally Measured Extractable Material \( L \), Calculated Theoretical Amount of Extractable Material \( L \), Volumetric Swelling Ratio \( Q \), and Ethylene Glycol Fraction of the Dry Networks \( \phi_{EG} \) for PEG-PU Networks Containing mPEG Dangling Chains (NCO:OH = 1.1 for All Networks)

| PU network | PEG [g mol\(^{-1}\)] | mPEG [g mol\(^{-1}\)] | \( \text{OH}_{mPEG}:\text{NCO} \) | \( \text{exp L} \) [wt %] | \( \text{ideal theor L} \) [wt %] | \( Q \) [\( V/V_0 \)] | \( \phi_{EG} \) |
|------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|
| 1000       | 750               | 1:9               | \( \text{OH}_{mPEG}:\text{NCO} = 1:9 \) | 0.67 ± 0.52       | 0.086             | 2.70 ± 0.02       | 0.724             |
| 2000       | 1:9               | 0.93 ± 0.07       | 0.165             | 3.21 ± 0.01       | 0.769             |
|            | 1:30              | 0.38 ± 0.01       | 0.005             | 2.58 ± 0.01       | 0.732             |
| 5000       | 1:9               | 0.291             | 0.724             | 4.42 ± 0.02       | 0.834             |
| 2000       | 750               | 1:9               | 0.32 ± 0.08       | 0.059             | 3.59 ± 0.01       | 0.829             |
|            | 1:30              | 0.15 ± 0.04       | 0.001             | 3.33 ± 0.02       | 0.831             |
| 2000       | 1:9               | 0.60 ± 0.33       | 0.117             | 3.97 ± 0.06       | 0.847             |
|            | 1:30              | 0.56 ± 0.56\( ^c \) | 0.003             | 3.40 ± 0.05       | 0.837             |
| 5000       | 1:9               | 0.96 ± 0.96\( ^c \) | 0.222             | 5.03 ± 0.03       | 0.878             |
|            | 1:30              | 0.40 ± 0.36       | 0.007             | 3.84 ± 0.01       | 0.849             |
| 6000       | 750               | 1:9               | 0.39 ± 0.01       | 0.028             | 4.94 ± 0.03       | 0.933             |
| 2000       | 1:9               | 0.67 ± 0.08       | 0.056             | 5.22 ± 0.01       | 0.935             |
|            | 1:30              | 0.18 ± 0.18\( ^c \) | 0.001             | 4.65 ± 0.01       | 0.937             |
| 5000       | 1:9               | 0.60 ± 0.19       | 0.115             | 5.75 ± 0.04       | 0.941             |
| 10000      | 2000              | 1:9               | 0.93 ± 0.33       | 0.038             | 5.95 ± 0.03       | 0.959             |
|            | 1:30              | 0.30 ± 0.13       | 0.001             | 5.55 ± 0.08       | 0.961             |
| 20000      | 750               | 1:9               | 0.55 ± 0.01       | 0.013             | 6.47 ± 0.02       | 0.978             |
|            | 1:9               | 0.83 ± 0.12       | 0.023             | 6.52 ± 0.02       | 0.978             |
|            | 1:30              | 0.70 ± 0.09       | 0.0004            | 6.66 ± 0.14       | 0.980             |
| 5000       | 1:9               | 3.25 ± 0.45       | 0.045             | 8.51 ± 0.16       | 0.979             |

\(^a\)Dry film thickness of all networks ± 120 \( \mu \)m. Every sample was made twice. The error represents the mean absolute deviation from the mean value. \(^b\)Unable to measure the amount of extractable material. \(^c\)Amount of extractable material of one sample undetectable. Therefore, only data of the other sample was used.

Figure 4. Mean volumetric swelling ratio \( Q \) of PEG-based PU networks with varying diol network precursor \( M_\text{n} \) swollen to equilibrium in water. (a) Plotted against \( M_\text{n} \) for networks without mPEG (squares) and with mPEG 2000 [g mol\(^{-1}\)] OH\( _{mPEG}:\text{NCO} = 1:9 \) (solid circles) or OH\( _{mPEG}:\text{NCO} = 1:30 \) (open circles). (b) Plotted against the total PEG fraction in the network \( \phi_{EG} \) for networks with different \( M_\text{n} \) of the PEG-diol precursor (colors) and with or without mPEG of different molar mass (symbols) for networks with OH\( _{mPEG}:\text{NCO} = 1:9 \). Trend lines for networks with similar mPEG masses are shown to aid the eye. The error bars show the mean absolute deviation.
Junctions

The error represents the mean absolute deviation from the mean value.

To OHmPEG:NCO = 1:9, a clear increase in dangling chains in a relative low amount of OHmPEG:NCO = 1:9 for all Networks

network model for the presence of additional defects, as will be used in the next section to correct the theoretical approach for a A\(_5\)A\(_3\)B\(_2\)B\(_1\) system. Nevertheless, since the

dangling chains in a relative low amount of OHmPEG:NCO = 1:9 for all Networks

amount of extractable material for most networks is still less than 1 wt %, the networks are considered to be suitable for a

precursor functionality into account. Moreover, since the

nor takes possible loop formation or deviations in effective precursor functionality into account. Nevertheless, since the amount of extractable material for most networks is still less than 1 wt %, the networks are considered to be suitable for a reliable comparison of the absolute swelling ratios between them. Moreover, the measured amount of extractable material will be used in the next section to correct the theoretical network model for the presence of additional defects, as explained in the previous section.

Figure 4a shows the effect of introducing mPEG dangling chains (\(M_\text{n} = 2000 \text{ g mol}^{-1}\)) on the volumetric swelling ratio \(Q\) of PEG-based PU networks with different \(M_\text{n}\) precursors. The respective networks without dangling chains are also shown for comparison. The figure shows that an addition of these mPEG dangling chains in a relative low amount of OH\(_{m\text{PEG}}\)NCO = 1:30 to the network structure does not significantly change the water uptake for networks prepared from precursors with \(M_\text{n} < 10000 \text{ g mol}^{-1}\). However, upon increasing the mPEG content to OH\(_{m\text{PEG}}\)NCO = 1:9, a clear increase in \(Q\) can be seen. These results indicate that for these networks only at high fractions of dangling chains a significant increase in water uptake can be expected, for which the relative contribution is largest for networks prepared from low-\(M_\text{n}\) PEG-diols.

Because tHDI is hydrophobic, the addition of mPEG dangling chains influences the overall fraction of hydrophilic material inside the networks. To see the actual network structural effect on the water uptake of these PEG-based PU networks, the networks are compared based on their overall ethylene glycol fraction \(\psi_{\text{EG}}\) in Figure 4b (colors represent different PEG-diol \(M_\text{np}\), whereas the symbols show the different mPEG \(M_\text{n}\), OH\(_{m\text{PEG}}\)NCO = 1:9). Obviously, the addition of mPEG has the largest effect on \(\psi_{\text{EG}}\) of PUPEG1000 networks (black). A comparison of the prepared networks based on their volumetric swelling ratio \(Q\) against \(\psi_{\text{EG}}\) shows no crossing of the sketched trend lines between networks prepared with similar mPEG \(M_\text{n}\) and an increase in water uptake upon increasing \(M_\text{n}\) of mPEG, regardless of the PEG-diol precursor used. Furthermore, the graph shows the possibility to significantly increase the swelling ratio of PEG-based PU networks upon addition of dangling network chains, thus many opportunities for designing networks with similar (or different) \(Q\) having a different (or similar) \(\psi_{\text{EG}}\).

Corrections Due to the Presence of Network Defects for the Calculation of \(M_c\). Next to the increase in overall water uptake, the addition of dangling chains to the network introduces network defects, as a dangling end can be seen as a defect itself. Moreover, the detection of extractable material after the network preparation indeed indicates the presence of additional defects since it exceeds the ideal theoretical amount of soluble material as shown in Table 3. These defects complicate an accurate calculation of \(M_c\). Therefore, it is proposed to account for these defects by adapting the ideal network structure relation using effective fractions of elastically active material \(\alpha\) and active cross-links \(\beta\), calculated by using the MMV approach, as explained at the beginning of this section. Table 4 gives the calculated values for \(M_c\) obtained by using the phantom model with ideal structure relations (eq 2), correction factors \(\alpha\) (eq 11) and \(\beta\) (eq 14), and the \(M_c\) from the corrected phantom model using these correction factors (eq 10) of the prepared PEG-mPEG-based PU networks.

### Table 4. Overview of \(M_c\) Calculated by Using the Standard Phantom Model Taking into Account the Allophanate Formation (Eq 2), Calculated Fractions of Effective Elastically Active Material \(\alpha\) (Eq 11), Calculated Effective Fraction of Active Network Functions \(\beta\) (Eq 11), and \(M_c\) Calculated Using the Corrected Phantom Model Taking into Account the Allophanate Formation (Eq 10) for PEG-PU Networks Containing mPEG Dangling Chains (NCO:OH = 1.1 for All Networks)

| PEG | mPEG | OH\(_{m\text{PEG}}\)NCO | mean \(M_\text{n}\) [g mol\(^{-1}\)] | phantom | \(\alpha\) | \(\beta\) | mean \(M_c\) [g mol\(^{-1}\)] | phantom corrected, \(f = 3.75\) |
|-----|------|-----------------|----------------|--------|------|------|----------------|----------------|
| 1000 | 750  | 1:9             | 956 ± 25       | 0.79 ± 0.05 | 0.79 ± 0.06 | 760 ± 12       |
| 1000 | 750  | 1:9             | 1597 ± 1       | 0.67 ± 0.01 | 0.79 ± 0.01 | 853 ± 10       |
| 1000 | 750  | 1:30            | 823 ± 7        | 0.84 ± 0.01 | 0.87 ± 0.01 | 669 ± 5        |
| 5000 | 1:9  | 1.95 ± 44       | 0.49 ± 0.3     | 82 ± 0.01  | 465 ± 6     |
| 2000 | 750  | 1:9             | 1217 ± 2       | 0.85 ± 0.01 | 0.80 ± 0.01 | 1946 ± 20      |
| 2000 | 1:9  | 1761 ± 39       | 0.91 ± 0.01    | 0.86 ± 0.01 | 1669 ± 50    |
| 2000 | 1:9  | 2710 ± 110      | 0.77 ± 0.02    | 0.80 ± 0.03 | 1967 ± 41    |
| 5000 | 1:9  | 1861 ± 93       | 0.86 ± 0.08\(^c\) | 0.86 ± 0.09\(^c\) | 1624 ± 42    |
| 5000 | 1:9  | 4422 ± 56       | 0.60 ± 0.01\(^c\) | 0.78 ± 0.02\(^c\) | 1766 ± 19    |
| 6000 | 1:9  | 2500 ± 5        | 0.83 ± 0.04    | 0.90 ± 0.05 | 1870 ± 47    |
| 2000 | 750  | 1:9             | 4241 ± 68      | 0.87 ± 0.01 | 0.77 ± 0.01 | 4216 ± 71     |
| 2000 | 1:9  | 4715 ± 30       | 0.83 ± 0.01    | 0.76 ± 0.01 | 4274 ± 56    |
| 5000 | 1:9  | 3772 ± 201      | 0.86 ± 0.01\(^c\) | 0.82 ± 0.01\(^c\) | 3588 ± 17    |
| 10000| 2000 | 1:9             | 5621 ± 78      | 0.78 ± 0.01 | 0.80 ± 0.02 | 4282 ± 11     |
| 2000 | 750  | 1:9             | 5962 ± 64      | 0.82 ± 0.03 | 0.73 ± 0.03 | 5548 ± 79     |
| 2000 | 1:9  | 6967 ± 46       | 0.83 ± 0.01    | 0.72 ± 0.01 | 6735 ± 112   |
| 5000 | 1:9  | 7240 ± 317      | 0.84 ± 0.01\(^c\) | 0.79 ± 0.01\(^c\) | 6613 ± 289   |
| 5000 | 1:9  | 10805 ± 386     | 0.69 ± 0.01    | 0.61 ± 0.02 | 8916 ± 189   |

\(^a\)Dry film thickness of all networks ± 120 \(\mu\)m. Every sample was made twice. Correction factors were obtained by using the MMV approach for a \(A_5A_3B_2B_1\) system. The error represents the mean absolute deviation from the mean value. \(^b\)Unable to measure the amount of extractable material. \(^c\)Amount of extractable material of one sample was undetectable. Therefore, only data of the other sample was used.
Again, the alloanate formation is taken into account in both models by using $f = 3.75$. The parameters $\alpha$ and $\beta$ are calculated based on an A5A3B2B1 system and the experimentally determined fraction of extractable material as given in Table 3. The mass of an A3 cross-linker molecule is taken as 549 g mol$^{-1}$ (based on the actual manufacturer value of the HDI used), whereas the mass of an A5 cross-linker molecule is simply taken as twice the mass of an A3 molecule in the calculations.

The $M_c$ calculated by using the standard phantom model for all networks with a high amount of mPEG chains (OHmPEG:NCO = 1:9) are shown versus the mPEG molar mass $M_n$ of the prepared networks when using the standard phantom model as can be seen in Figure 5a. From a structural point of view, by keeping the amount of dangling chains constant, a significant increase in $M_c$ is expected if only the length of the dangling chain is increased. This is particularly valid for networks of which both the PEG-diol and the mPEG chain are chosen with a $M_n$ below the $M_c$ of PEG, since this will interfere with the formation (or removal) of physically trapped entanglements in the network. However, Figure 5a shows different trends for the $M_c$ of the prepared networks when using the standard phantom model, given the observed mPEG $M_n$-dependent behavior. This shows that the standard phantom model is not able to predict an accurate $M_c$ for these kinds of networks.

On the other hand, this behavior is observed for the $M_c$ calculated from the corrected phantom model as can be seen in Figure 5b, in which a clear mPEG $M_n$-independent behavior can be seen for the networks prepared with PEG-diol with $M_n \leq 6000$ g mol$^{-1}$. The calculated $M_c$ for the PUPEG10000, -20000, and -60000 networks with mPEG chains of 750 and 2000 g mol$^{-1}$ is slightly larger than the reference, as expected, since the presence of dangling chains reduces the amount of active cross-links when reacted with a 3-functional cross-linker (i.e., if a dangling chain reacts with a 3-functional cross-linker, the maximum amount of chains by which the cross-linker molecule is connected to the infinite network structure is less than 3 and therefore no longer an active cross-linking point). At the same time the total mass of the other two connected chains plus the mass of the cross-linker molecule itself is still elastically active material and thereby effectively increasing the overall $M_c$ of the network. The slight decrease of apparent $M_c$ for these networks with an mPEG of 5000 g mol$^{-1}$ is believed to be due to the formation of physical entanglements, since this precursor has a $M_n$ above the $M_c$ of PEG. The increase in $M_c$ for PUPEG10000 and -20000 networks can be explained by exactly the opposite effect, since in these networks a fraction of the high-$M_n$ PEG-diol is "replaced" by a low-$M_n$ mPEG. Hereby, the amount of trapped physical entanglements is reduced, which leads to an overall higher value for $M_c$. Only the larger increase in the PEG200000-mPEG50000 networks seems to be overestimated. It should be noted that these networks showed a significantly higher amount of extractable material (3.25 wt %) (see Table 3) compared to all other networks (<1 wt %). Also, the fact that the swelling ratios of these networks were relatively higher provides confidence that this larger calculated $M_c$ is real and due to more defects in these networks and not an error or limitation in the calculation method.

Finally, we need to address the effect of incomplete conversion, as treated by Lang et al., and the effect of loops, as has been recently treated by Zhong et al. and Lang. Incomplete polymerization leads to a lower value for the cycle rank per chain than the ideal $\zeta = 0.5$ for copolymerization, a typical estimate for $f = 4$ being $\zeta = 0.314$ for a conversion of 0.875. From the fact that the amount of extractable material in our case is on average about 0.6%, we infer that the conversion is about 99.4%. This leads to a negligible effect of about 1% on the modulus. For the effect of loops the two treatments essentially agree, although there are minor differences, which have been discussed by Lang. The effect of loops is the largest for the smallest loops and the smallest molecular weight, i.e., for the PEG1000 system. Using the relevant data, the fraction of loops can be estimated to be about 4%, leading to a decrease in modulus by a factor of about 0.96. For larger molecular weights this factor will be even closer to 1. Overall, these corrections are thus negligible.

Overall summarizing, we conclude that although the introduction of mPEG dangling chains introduces a change in polymer–solvent interaction, below the entanglement length the phantom network model describes the behavior well while clear reasons why above the entanglement length slight deviations occur have been elaborated in the discussion above.
CONCLUSIONS

The influence of the PEG-diol network precursor mass on the swelling ratio and network formation of hydrophilic PEG-based PU networks is studied, both experimentally and theoretically. Moreover, the study is extended to the influence of the presence of mPEG dangling network chains in the swollen networks. A suitable network preparation procedure is found to obtain networks that contain no residual NCO groups, amounts of extractable material below 1 wt %, and showed no tendency to curl.

The swelling behavior of PEG-based PU networks in water is best described by the phantom network, as expected. To calculate an accurate value for $M_c$ of the prepared networks from the measured water uptake, allophanate formation, as shown to be present by swollen state $^1$H NMR, needs to be taken into account when assigning the overall junction functionality of the networks (i.e., $f = 3.75$ in this work). Taking this into account the phantom model yields values for $M_c$ which indicate a near-ideal network formation for low-$M_c$ precursors (slope = 0.88), while the use of higher $M_c$ precursors gives rise to the formation of trapped physical entanglements (slope = 0.12). The transition point from the near ideal regime to the entangled regime is found to coincide with the molar mass of PEG at which entanglements are formed in the melt ($M_e$). Although it is known that physical entanglements suppress the swelling of swollen polymer networks and increase their modulus, this is to the best knowledge of the authors the first time that this transition point is shown for swollen PU networks using a set of well-defined networks.

The addition of dangling chains to PEG-based PU networks will increase the swelling ratio of the networks, regardless of the PEG-diol precursor used. This allows some freedom in the design of hydrophilic networks with varying water uptake capabilities and network architectures. Furthermore, when comparing the swelling ratios of the mPEG containing networks with the actual content of hydrophilic material in the network, clear trends in swelling ratio for different dangling chain masses are found. Most notably, it is shown to be of utmost importance to correct for network imperfection when using standard network swelling models to calculate the $M_c$ for these PEG-mPEG PU networks. This is essentially true for all polymeric networks prepared via end-linking polymerization reactions. The proposed corrections to the classical ideal network structure relations in combination with the statistical Miller–Macsosko–Vallés approach to calculate overall network structure factors are shown to be able to predict an accurate value for the $M_c$ of these swollen PEG-based PU networks containing high amounts of dangling network chains. This provides a new approach for studies which require an accurate estimate of $M_c$ only based on experimentally straightforward swelling experiments.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.macromol.9b02275.

Brief review of the theory of polymeric network swelling; influence film thickness and solid weight content formulation on the swelling ratio; discussion on allophanate formation; and influence $\chi$ on $M_c$ and the Miller–Macsosko–Vallés recursive probability approach (PDF).

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Notes

The authors declare no competing financial interest.

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