



Soft Matter

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Journal:	<i>Soft Matter</i>
Manuscript ID	SM-ART-04-2020-000747.R1
Article Type:	Paper
Date Submitted by the Author:	31-May-2020
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Aqueous polypropylene glycol induces swelling and severe plasticization of high T_g amphiphilic copolymers containing hexafluoroisopropanol groups

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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Poly(ethylene glycol) (PEG) tends to be considered low fouling, which has led to its use in a wide variety of applications. Amphiphilic polyols, such as Antifoam 204, are commonly used as surfactants in fermentation processes due to their limited toxicity and low cost, but these polyols in aqueous solutions can unexpectedly swell membranes. Here we examine the interactions of PEG or poly(propylene glycol) (PPG) with amphiphilic substituted norbornenes copolymers through swelling in dilute aqueous solution. The effect of molecular mass (M_n) of the polyol (PEG and PPG) in aqueous (1 wt% butanol) solution on the swelling and mechanical properties of a series of poly(alkyl norbornene-co-hexafluoroisopropanol norbornene) copolymers is systematically investigated using quartz crystal microbalance with dissipation. At 10 ppm of PEG, the swelling is less than 20 % for all of the copolymers examined and the swelling is independent of PEG M_n . In contrast, although PPG at the lowest M_n examined leads to similar swelling as PEG, the swelling induced by PPG increases with M_n to reach a maximum at $M_n = 3.1$ kg/mol. Pluronic L121 is similar compositionally to Antifoam 204, but the equilibrium swelling is decreased by a nearly factor of 2. These results suggest that the interactions between the polyol and hexafluoroisopropanol moiety in the copolymer drives the uptake by the membrane through bound water with the unassociated ether in the PPG that leads to substantially increased swelling with increasing M_n , but there is a finite size effect that limits the swelling in sufficiently large polymer additives.

Introduction

Polymeric membranes offer a low-cost and energy-efficient path for separation.¹⁻⁴ From a sustainability perspective, these membranes are particularly attractive for the separation of biologically derived products with high boiling points from fermentation broths due to the high energy costs associated with distillation of dilute aqueous solutions.⁵ Generally the interactions between the biological components, including byproducts of the biorefinery, can lead to undesired fouling that adversely impacts the performance of the membranes.⁶ The design of polymers for biological membrane separations thus must not only provide high permeance and selectivity for the desired product, but also be resistant to fouling by the complex mixture that comprises the fermentation broth.

For transportation fuels, there has been significant interest in recent years to develop organisms that preferentially produce butanol to replace the common bioethanol fuel additive due to

the higher energy density of butanol and lower water solubility in butanol to improve compatibility with the fuel delivery infrastructure.⁷⁻¹⁰ Beyond the challenges associated with engineering microorganisms to preferentially produce butanol,¹¹ the low feasible titer concentration due to cytotoxicity and the higher boiling point of butanol than water creates a separation challenge as distillation is not economical.^{8, 12, 13} Pervaporation membranes represent one of the most promising solutions for the separation challenge,¹⁴ but identification of potential low cost, high performance polymeric materials for these membranes has been challenging.^{14, 15} Recently, Register and coworkers identified a family of copolymers based on the addition polymerization of functionalized norbornene monomers that exhibit promising performance for the separation of neat butanol-water mixtures.^{16, 17}

We have recently reported on the swelling of one analogous copolymer when ppm levels of a common surfactant for controlling foam in fermentation broths, Antifoam 204, is added to the solution.¹⁸ Even at 1 ppm, the Antifoam 204 leads to >50% swelling of the copolymer and severe plasticization that will adversely impact the membrane performance.¹⁸ However, it is unclear if there are simple routes to modify the surfactant used or the membrane copolymer to overcome this undesired swelling to enable these copolymers to be used for separations in biorefineries.

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Electronic Supplementary Information (ESI) available: GPC traces, raw QCM-D data for swelling, fits of QCM-D data to power law model are included. See DOI: 10.1039/x0xx00000x

Here we systematically investigate the role of hydrophobicity and molecular mass of the polyol using *in-situ* quartz crystal microbalance with dissipation (QCM-D) to quantify both the swelling and rheological properties (where possible). Systematic variation from methyl to decyl for the alkyl chain length in poly(alkyl norbornene-co-hexafluoroisopropanol norbornene) was used to understand how the hydrophobic anchoring group influences the copolymer swelling by aqueous polyols. These polyols included a series of well-defined poly(ethylene glycol) (PEG) and poly(propylene glycol) (PPG) standards of varying molecular mass. The alkyl chain length on the copolymer did not dramatically influence the swelling. Conversely, the swelling was strongly dependent on the additive details: limited swelling was induced by PEG, while significant swelling was observed with higher molecular weight PPG at a fixed 10 ppm. The swelling by the PPG was molecular weight dependent with a maximum in the swelling at ≈ 3 kg/mol, which is similar to the molecular weight of Antifoam 204 that leads to ≈ 10 vol% copolymer in the swollen state.¹⁸ To better understand the molecular weight effect, a series of Pluronic surfactants with varied molecular weight and composition was also examined. Even with a similar composition to Antifoam 204, the swelling decreased by nearly a factor of 2 with Pluronic L121, which has a larger molecular weight. These results indicate that the size of the polymer (as determined from GPC) is the critical factor that controls the swelling of these amphiphilic copolymer films. These results may not only be useful for selection of Antifoam agents for biobutanol membranes, but also potentially helpful to understand fouling behaviour with amphiphilic conetworks¹⁹ and other amphiphilic coatings.

Experimental Section

Materials. 1-butanol ($\geq 99.4\%$, ACS reagent), toluene ($\geq 99.5\%$, ACS reagent), tetrahydrofuran (THF, $\geq 99.5\%$, ACS reagent), Antifoam 204, and Pluronic® L121, F108, F127 were obtained from Sigma-Aldrich and used as received. Poly(propylene glycol) (PPG) and poly(ethylene glycol) (PEG) standards with narrow molecular mass distributions were purchased from Scientific Polymer Products, Inc. All aqueous solutions were prepared using Type 1 ultrapure water (Milli-Q direct water purification system, Millipore).

Table 1. Characteristics of the statistical copolymers.

Copolymer	M_n (kg/mol)	\bar{D}	X_{HFANB}
MeNB-r-HFANB	194.2	2.0	0.51
BuNB-r-HFANB	235.3	2.5	0.53
HeNB-r-HFANB	209.0	2.2	0.49
DeNB-r-HFANB	221.6	2.4	0.51

The copolymers examined herein were obtained from Promerus, LLC (Brecksville, OH). The polymers were synthesized by catalyzed addition co-polymerization of an n-alkyl norbornene and hexafluoroisopropyl norbornene

(HFANB). The alkyl group was systematically varied from methyl norbornene (MeNB) to butyl norbornene (BuNB) to hexyl norbornene (HeNB) to decyl norbornene (DeNB). All of the copolymers were determined to contain approximately 50 mol% HFANB by ^{13}C NMR. Table 1 provides the molecular weight information about these copolymers. As previously reported by ^1H NMR,¹⁸ Antifoam 204 contains 85.5 mol% PPG and 14.5 mol% PEG. Figure 1 illustrates the chemical structure of the norbornene copolymers examined as well as the two model additives, PEG and PPG.

Film Fabrication. Films of the copolymers were cast from a mixture of toluene:THF (1:1 wt:wt) by spin coating. This mixture was used previously to produce high quality membranes of BuNB-HFANB for butanol separation.^{16, 20} It should be noted that the membrane (film) preparation was different with knife casting used for the membranes and spin casting here for the QCM-D measurements, which may impact the quantitative swelling due to differences in chain conformation. The copolymer concentration in solution was used to vary the film thickness from approximately 40 nm to 1800 nm. Films were cast onto cleaned quartz crystal sensors (QSX-301, Q-Sense) with a gold surface (Figure 1). The sensors were cleaned by sequential sonication (VWR, Symphony Ultrasonic Cleaner) in toluene, isopropanol and ultrapure water for 30 min. After sonication in water, the sensor was blown dried with a N_2 gas stream using a cleanroom-rated gas gun (TA-N2-2000FT, NCI). Finally, ultraviolet-ozone treatment (UVO CLEANER, Model 42, Jelight Company Inc.) for 90 s was applied to remove any possible residual organics. The nominal fundamental resonant frequency was 5 MHz for these sensors. The copolymer films were cast on the clean sensors by spin coating (WS-400B-6NPP/LITE, Laurel Technologies) at 2500 rpm for 50 s and dried at 90 °C under vacuum (>28 Torr) for 1 h to remove any residual solvent prior to characterization.

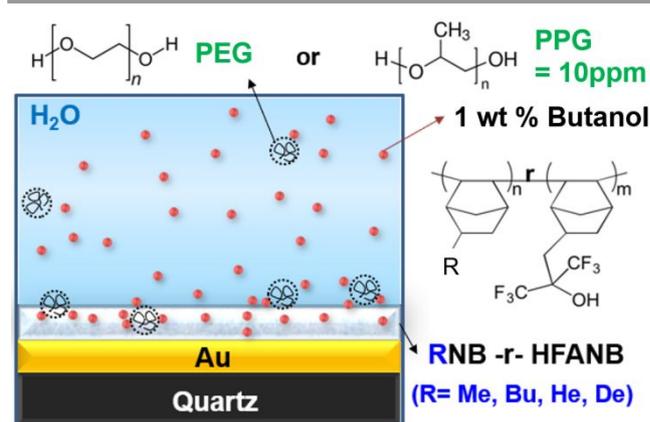


Figure 1. Schematic illustrating the geometry for the QCM-D measurements. The copolymers with varying alkyl side groups were spin cast on the gold coated quartz sensor. Immersion in aqueous solutions containing 1 wt% n-butanol and 10 ppm of PEG or PPG leads to swelling of the copolymer film that is assessed by QCM-D.

Characterization.

Gel permeation chromatography (GPC). A Tosoh EcoSEC HLC-8320 GPC with a Refractive Index (RI) detector was used to assess the molecular weight of PEGs and PPGs. THF was used as the eluting solvent. The molecular weights are reported relative to polystyrene standards. Figure S1 illustrates the GPC traces for the series of PEG and PPG examined. The molecular weights determined from GPC correspond well to the nominal reported molecular weights for $M_n < 1500$ g/mol, but the measured molecular weight tends to be greater than the nominal molecular weight with this deviation growing as molecular weight increases for PPG. The molecular weight reported within the text of the manuscript corresponds to the measured M_n . Table 2 quantifies the molecular weight and its distribution for the polyols examined.

Table 2. Comparison of the nominal and measured molecular weights of the polyols

Polyol	Nominal M_n (Da)	GPC M_n (Da)	GPC \bar{D}
PEG	900	920	1.07
PEG	2890	3480	1.08
PPG	440	460	1.11
PPG	1020	1330	1.10
PPG	2050	3120	1.08
PPG	2870	4090	1.09
Antifoam	-	3240	1.07

Swelling and viscoelastic properties by QCM-D. All quartz crystal microbalance with dissipation (QCM-D, Q-Sense Analyzer, Biolin Scientific) measurements were performed at 37 °C to obtain shifts in frequency (Δf) and dissipation ($\Delta \Gamma$) that result from exposure to aqueous solutions. The swelling was measured using QCM-D sensors coated with a film of the copolymer of interest. The film was subsequently exposed to aqueous solution that was slowly pumped over the surface of the sensor as schematically shown in Figure 1. As the sensor is impermeable, no separations occur during the swelling experiment, but the copolymer films in general can equilibrate against the known solution.

For analysis of the QCM-D data, the 3rd (15 MHz) and 5th (25 MHz) overtones were used. The Δf and $\Delta \Gamma$ of the coated sensors were calculated relative to the uncoated sensors in the same environment (air, water, or butanol solution). The responses of the QCM-D observed in this work can be summarized schematically in Figure 2. The addition of the copolymer coating adds relatively rigid mass to the quartz to reduce the frequency of the oscillation from the uncoated sensor (Figure 2a), but the energy loss remains low, so the time dependent dampening of the amplitude is only marginally increased for thin films (Figure 2b). This allows for the dry film thicknesses in air to be calculated directly from $\Delta f_{\text{dry film}}$ using the Sauerbrey equation,²¹ when the energy loss for the glassy polynorbornene is negligible (films thinner than approximately 1 μm).²² The norbornene copolymer films were swollen at 37 °C by drawing the desired aqueous solution through the flow

module (QFM 401, Biolin Scientific) using a peristaltic pump (Ismatec IPC-N 4) at 50 $\mu\text{L}/\text{min}$. The properties of the swollen film after sorption of components from the solution were determined by the experimentally measured Δf and $\Delta \Gamma$ between coated and uncoated sensors. The QCM-D response to the fluid is two-fold. First the fluid phase alone will lead to a shift in both the frequency and dissipation due to the fluid properties (density and viscosity). Swelling of the coated film will alter its effective mass and rheology (as film is adhered to the sensor) to lead to additional shifts. Combined these effects tend to dramatically decrease the frequency and more rapidly dampen the oscillations as illustrated in Figure 2c. In this work, Δf and $\Delta \Gamma$ are corrected for the solvent effect alone by exposing an uncoated sensor to the same solution. The addition of the PPG or Antifoam at 10 ppm in 1 wt % butanol (aqueous) leads to additional swelling to significantly increases the dissipation (Figure 2d). In all cases, the films were allowed to equilibrate until Δf for both the 3rd and 5th overtone changed < 6 Hz/h where possible.

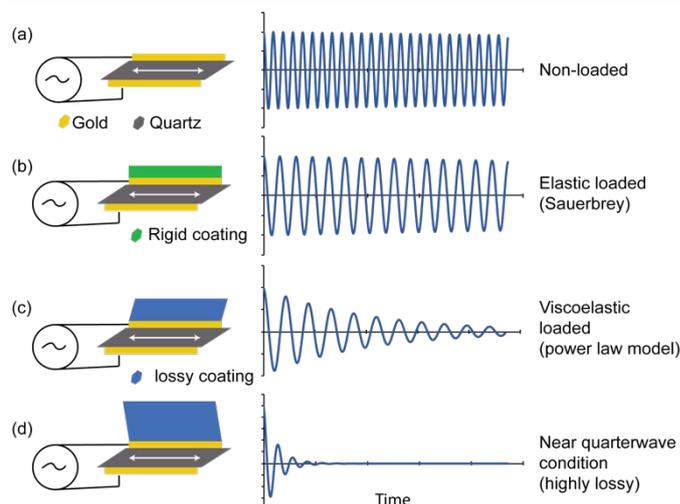


Figure 2. Schematic illustrating the different regimes of operation of the QCM-D observed in these studies. The QCM-D operates in the time domain and the decay in the oscillation after switching off the A/C current is indicative of energy dissipation. (a) The uncoated sensor exhibits a high frequency and low energy dissipation. (b) For sufficiently thin films, the coating appears rigid whereby the added mass decreases the oscillation frequency without significant change in energy dissipation. (c) When the viscous losses are appreciable, an increased decay in the amplitude due to energy dissipation is observed. (d) For sufficiently thick coatings with high loss, the frequency can increase with additional swelling while there is a large increase in energy dissipated such that it can be challenging to determine the frequency.

For the examination of the effect of the polyols, the initial exposure to 1 wt% butanol solution enabled the effect of the additive to be clearly separated in each case. After exposure to any solution containing an additive, the films were not re-used for other experiments as the additive could not be readily removed from the film consistent with previous report for Antifoam 204.¹⁸ The inclusion of the additive leads to long equilibration times as shown in Figure S2. In some cases, the film appears to be adding mass even after 18 h. For thicker films, the large swelling induced by some of the additives can

lead to significant dampening of the oscillation, such that the frequency cannot be accurately determined (no signal). In these cases, the measurement was stopped prior to reaching equilibrium. The average frequency shifts and dissipation change over last 60 min were used for determining the equilibrium or measurement limit (due to dampening of the quartz oscillation) properties of films swollen by solutions containing additives.

For control experiments, n-butanol solutions that were free of the PPG/PEG additives were introduced sequentially (0, 1 wt%, 2 wt%, and 3 wt%) to determine the effect of n-butanol concentration on the swelling and mechanical properties. Each concentration examined was allowed to reach equilibrium (defined as $\Delta f < 6$ Hz/h) with the equilibrium frequency and dissipation change reported as the average of the last 10 min of measurements. Typically, approximately 1 h was required to reach equilibrium for these solutions without additive. Figure S3 illustrates representative data for swelling of the copolymers with butanol/water solutions. These come to equilibrium rapidly in comparison to when polyols are present in solution.

QCM-D data analysis. The swelling data from QCM-D were analyzed with a self-consistent, power law model.²³⁻²⁷ This model uses the frequency and dissipation changes at 3rd and 5th overtones to self-consistently solve the wave propagation to recursively fit the frequency and dissipation changes²³ with the assumption that the storage and loss moduli exhibit a power-law frequency dependence.²⁴ The change in dissipation factor, ΔD , which is utilized in the time-domain QCM-D technique, is directly related to the half bandwidth, $\Delta \Gamma$, as: $\Delta D = 2\Delta \Gamma / \Delta f$.²⁸ Here, $\Delta \Gamma$ is presented throughout for consistency with prior publications using the power law model.²³⁻²⁵ A perfect match of $\frac{3}{4}$ of the parameters (Δf_3 , Δf_5 , $\Delta \Gamma_3$, $\Delta \Gamma_5$) between the fit values and the experimental measurements is the criterion for convergence and acceptance of the fit parameters.²³ In order to obtain rheological properties from QCM-D, the energy loss of the sensor must be sufficient, which depends on the thickness of the film as well as the rheological properties.²⁴ Thus for the thinner films and less swollen films, only swelling properties (mass or thickness) are obtainable. From the power-law model fit, three physical parameters that describe the films are obtained: film thickness (h), the product of density and magnitude of the complex shear modulus determined for the 3rd overtone (ρ/G^*), and the phase angle (ϕ). The meaning of phase angle here is from solid mechanics where $\phi = 0^\circ$ for a fully elastic material and $\phi = 90^\circ$ for a fully viscous material.

Results and discussion.

Exposure of the copolymer films to aqueous butanol solutions leads to swelling of the copolymer as evidenced by the decrease in frequency and increase in energy dissipation as shown in Figure S3. The decreased frequency is consistent with added mass within the Sauerbrey regime, while the increase in

dissipation indicates that the viscous losses during the oscillation of the quartz increase as would be expected from plasticization of the copolymer by the solvent. The frequency and dissipation shifts can be readily fit to the power law model (Figure S4) to determine the thickness and rheological characteristics of the films at swelling equilibrium. The influence of butanol concentration on the swelling of the four copolymers with systematically varied alkyl side chains on the hydrophobic monomer is shown in Figure 3a. The change in the thickness at equilibrium (h) from the initial film thickness (h_0) is normalized by the equilibrium thickness. As the swelling is effectively unidirectional due to the adhesion of the film to the substrate, so this normalized thickness is effectively the volume fraction of solvent within the polymer film. As the butanol concentration increases, there is a commensurate increase in the swelling of the copolymer film. As the alkyl chain length on the copolymer is increased, the swelling decreases irrespective of the butanol concentration. The effect of the alkyl length on the equilibrium swelling increases as the butanol concentration increases.

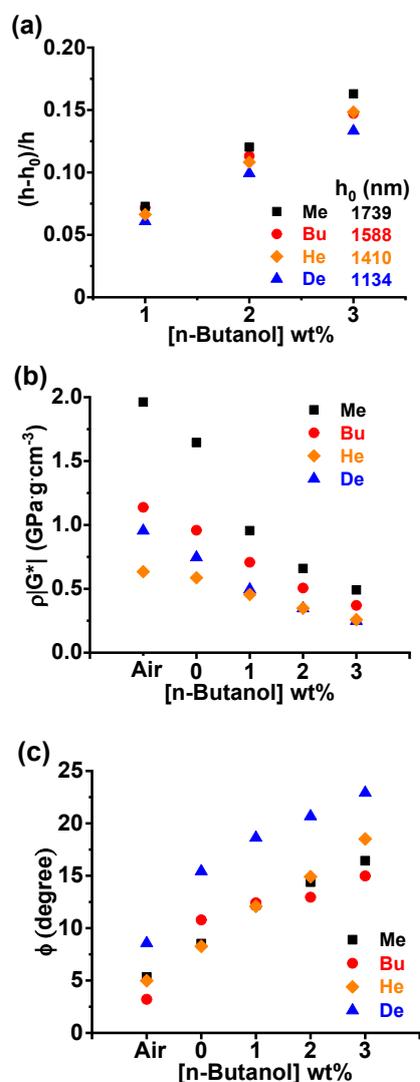


Figure 3. Impact of butanol concentration on the equilibrium (a) volumetric swelling $[(h-h_0)/h]$, (b) product of the density and magnitude of the complex

shear modulus (ρ/G^*) and (c) phase angle (ϕ) for films of random copolymer of hexafluoroisopropyl norbornene and alkyl polynorbornene (RNB-r-HFANB, R= Me, Bu, He, and De). Dry film thicknesses (h_0) for the copolymers with methyl, butyl, hexyl, and decyl norbornene are 1739 nm, 1588 nm, 1410 nm, and 1134 nm, respectively.

Relatively thick films (1-2 μm) were used to ensure sufficient energy dissipation to allow for accurate determination of the rheological properties of these swollen films by QCM-D.²³ As shown in Figure 3b, the modulus decreases as the swelling increases (as the density difference between the swollen and non-swollen state should be small). In air, ρ/G^* decreases from nearly 2 $\text{GPa}\cdot\text{g}\cdot\text{cm}^{-3}$ for MeNB-HFANB to approximately 0.6 $\text{GPa}\cdot\text{g}\cdot\text{cm}^{-3}$ for HeNB-HFANB. The difference in ρ/G^* between copolymers is less when swollen with butanol solution, which is consistent with the modest increased swelling for the copolymers with shorter alkyl chains (Figure 3a) that will increase the plasticization. This plasticization of the copolymers by butanol is also consistent with the change in the phase angle associated with the sorption. As shown in Figure 3c, the phase angle increases as the butanol concentration in the solution increases, which indicates that the films dissipate more energy when swollen (larger relative loss modulus). However even when equilibrated against 3 wt% butanol solution, the phase angle is less than 25° and thus these copolymers remain viscoelastic solids in the swollen state.

The addition of polyols at 10 ppm increases the swelling of the copolymer film as shown in Figure 4 for thin BuNB-HFANB films. As Antifoam 204 tremendously swells this copolymer,¹⁸ relatively thin BuNB-HFANB films (dry thickness $h_0 = 44 \pm 2$ nm) were examined to avoid challenges with the dampening of the QCM-D signal by the addition of the polyols. Figures S5-S11 show the time dependent response of the QCM-D for swelling with the different polyols at 10 ppm. As shown in Figure 4, the swelling with neat 1% butanol is increased markedly over the swelling observed in much thicker films at the same concentration (Figure 3a). This increased swelling was consistent for all of the films examined (see open symbols in Figure 4 for the neat 1% butanol), which suggests finite thickness effects for the swelling as has been observed in other polymer-solvent systems.^{29, 30} For these thin films, the addition of either PPG and PEG at 10 ppm modestly increases the volumetric swelling over the neat 1% butanol. The monomers (ethylene and propylene glycol) appear to increase the swelling by a similar extent. As the molecular weight is increased, a notable difference between PEG and PPG for their influence on swelling is observed. The volumetric swelling of the BuNB-HFANB by 10 ppm PEG is independent of the molecular weight, while the swelling of the BuNB-HFANB increases as the molecular weight of PPG increases. However, the swelling induced by PPG and PEG at 10 ppm for the molecular weights examined is significantly less than observed with Antifoam 204 ($M_n = 3240$ g/mol). A copolymer of PEG and PPG appears to exhibit swelling substantially greater than the individual components for the BuNB-HFANB. The much lower swelling observed for the PPG and PEG than Antifoam at 10

ppm leads to limited energy dissipation to prohibit accurate assessment of the rheological properties of these swollen films due to their limited thickness ($h_0 = 44 \pm 2$ nm).

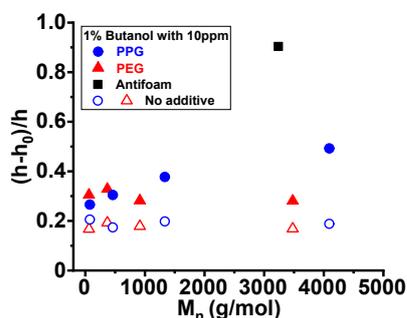


Figure 4. Effect of additive composition (PPG/PEG) and its M_n on the swelling of BuNB-HFANB films ($h_0 = 44 \pm 2$ nm) in 1% butanol with 10 ppm additive. The control measurements for each film in neat 1% butanol solution are shown with the open symbols. The rheological properties were not reported due to low d/λ for all cases except Antifoam 204.

In order to better understand how the additional swelling from the PPG influences the rheological properties of the copolymers, thicker films ($h_0 = 288 \pm 15$ nm) were examined with MeNB-HFANB. The time dependent QCM-D data along with their fits for these films are shown in Figures S12-S17. The switch from butyl to methyl should decrease the hydrophobicity of the system to increase the swelling, while the modulus of the dry MeNB-HFANB is the largest for the copolymers examined (Figure 3b) to illustrate the potential impact of these additives on the mechanical properties. Figure 5a illustrates how the swelling depends on the molecular weight of PPG. For propylene glycol, there is only a slight increase in the swelling in comparison to the neat butanol solution. The swelling increases as the molecular weight of the PPG increases initially. At $M_n = 3120$ g/mol for the PPG, the QCM signal is dampened completely during the sorption (see Figure 2d) to prohibit the equilibrium swelling from being measured. The change in frequency and dissipation just prior to loss of signal provides a lower bound for the swelling as shown by the open symbol in Figure 5a. When the molecular weight is further increased, there is a decrease in the swelling and there are no issues with overdampening of the crystal (signal loss). This indicates that there is a maximum in the swelling that occurs when the PPG molecular weight is approximately 3.1 kg/mol. Interestingly the Antifoam 204 ($M_n = 3240$ g/mol) has a very similar molecular weight to PPG ($M_n = 3120$ g/mol), the high extent of swelling fully dampens the oscillations (no signal) prior to reaching equilibrium when 10 ppm of Antifoam 204 is used. The swelling at which the signal is lost is similar between Antifoam 204 and PPG ($M_n = 3120$ g/mol), which suggests that the plasticization of the copolymer is similar by these two additives.

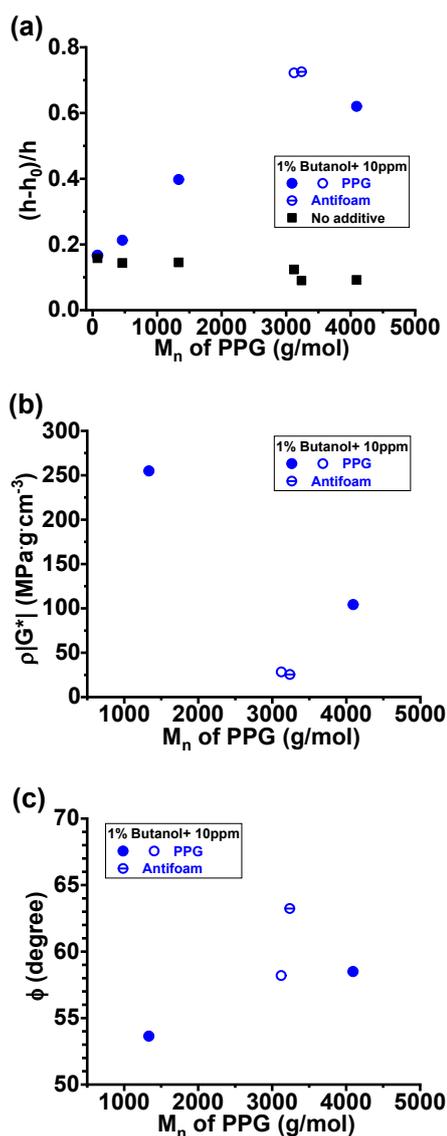
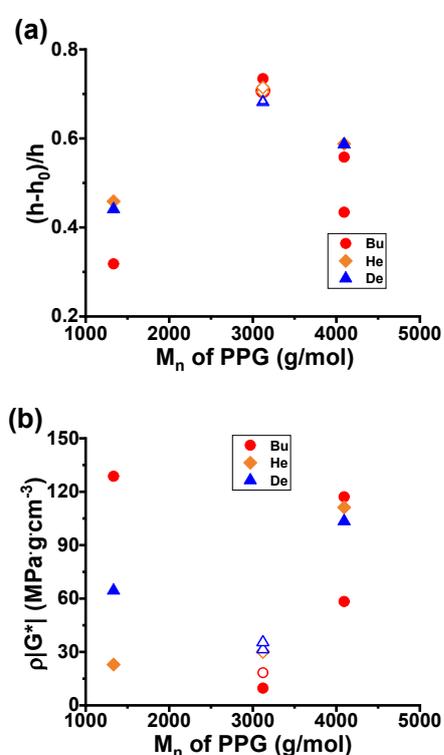


Figure 5. Impact of PPG molecular weight on the (a) volumetric swelling $[(h-h_0)/h]$, (b) product of the density and magnitude of the complex shear modulus $(\rho|G^*|)$ and (c) phase angle (ϕ) for MeNB-HFANB films ($h_0=288 \pm 15$ nm). For both Antifoam and the PPG with similar M_n , these films did not reach equilibrium prior to overdamping and loss of signal as denoted by the open symbols. The final data obtained are shown with the open symbols. It should be noted that these are the lower limit for swelling and ϕ , while the upper limit for $\rho|G^*|$.

With the thicker film examined, the influence of the PPG additive at 10 ppm on the mechanical properties of the MeNB-HFANB films can be assessed in some cases. As shown in Figure 5b when the swelling equilibrium was reached (solid symbols), there is an approximately one order of magnitude decrease in the modulus with the addition of PPG in comparison to the MeNB-HFANB in neat 1% butanol solution (Figure 3b). Despite only 10 ppm of PPG in the 1% butanol solution, this modulus is still nearly half that obtained when the MeNB-HFANB is equilibrated with 3% butanol. Figure 5c illustrates the phase angle determined from the QCM-D measurements. Despite the high T_g for the copolymer (>300 °C), the phase angle increased to $>50^\circ$ after sorption of the 10 ppm PPG solution. This is indicative of a viscoelastic liquid ($>45^\circ$) even at the high

frequency (MHz) associated with the QCM. Even using 3 wt% butanol, the phase angle barely increased above 15° , consistent with a glassy film. These results illustrate that PPG is a highly effective plasticizer for the MeNB-HFANB copolymer.

To better understand the maximum in swelling with PPG ($M_n = 3120$ g/mol), the series of copolymers was examined for 3 molecular weights of PPG while using similar thickness films. Figure 6a illustrates that the same maximum in swelling occurs for all of the copolymers. For all of the copolymers, equilibrium was not reached with solutions containing 10 ppm of PPG ($M_n = 3120$ g/mol), similar to that shown previously with MeNB-HFANB. The swelling is less for the BuNB-HFANB in the cases where equilibrium was obtained. When examining the order associated with the swelling of PPG ($M_n = 3120$ g/mol), this corresponds with the thicknesses of these films; the BuNB-HFANB is the thinnest and thus must swell more before signal loss. The mechanical properties of these films are significantly impacted by the sorption of PPG with an order of magnitude reduction in modulus (Figure 6b) in comparison to the modulus in neat 1% butanol (Figure 2b). As shown in Figure 6c, the phase angle is also significantly increased with most of the films appearing to be viscoelastic liquids. Interestingly, the HeNB-HFANB tends to exhibit lower phase angles, suggesting that this copolymer is less susceptible to plasticization by the PPG. This is likely associated with the hydrophobicity of the hexyl side chains to limit the PPG affinity, while the hexyl is not too long to adversely impact the mechanical properties of the neat copolymer unlike DeNB-HFANB (Figure 3c).



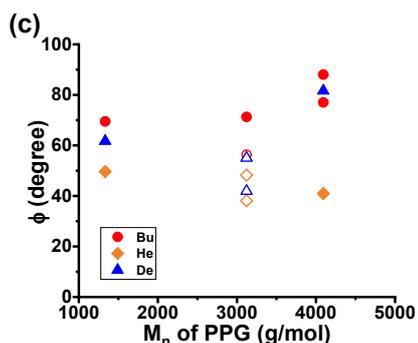


Figure 6. Effect of PPG molecular weight (measured value) and sidechain length of polynorborene on the (a) volumetric swelling $[(h-h_0)/h]$, (b) product of the density and magnitude of the complex shear modulus (ρ/G^*) and (c) phase angle (ϕ) for BuNB-HFANB ($h_0=225 \pm 36$ nm), HeNB-HFANB ($h_0=309 \pm 17$ nm) and DeNB-HFANB ($h_0=318 \pm 24$ nm).

To better understand the effect of the additive chemistry, the series of copolymers were swollen by 10 ppm of PEG, PPG, and Antifoam 204 with similar M_n . As these molecular weights are determined from GPC relative to PS standards, it is actually the hydrodynamic radius of these polymers that are similar. As shown in Figure 7, the alkyl chain length in the copolymer does not dramatically influence the swelling properties with these polyols. However, there is a significant difference between the PPG/Antifoam 204 and PEG. The PEG at 10 ppm leads to limited swelling in comparison to the other two polyols. For PPG and Antifoam 204, the swelling is sufficient that the QCM-D signal is fully dampened prior to reaching equilibrium. The swelling is <20% with 10 ppm PEG, while >65% with 10 ppm PPG or Antifoam 204 (the values reported in Figure 7a are the minimum), irrespective of the copolymer composition. This difference in swelling leads to an order of magnitude difference in the modulus (Figure 7b). For the copolymers swollen with the butanol solution containing PEG, the dissipation was insufficient to accurately assess the mechanical properties for the copolymers with short alkyl chains. The mechanical properties of DeNB-*r*-HFANB and HeNB-*r*-HFANB when swollen with neat 1 wt% butanol are very similar (Figure 3b), but the modulus of DeNB-*r*-HFANB is appreciably lower than that of HeNB-*r*-HFANB with the addition of 10 ppm of PEG. These differences also are observed in the phase angle (Figure 7c) where the phase angle for the DeNB-*r*-HFANB is approximately 45° after swelling with 10 ppm PEG. This increase in the phase angle despite the limited swelling is consistent with results shown in Figure 6c, where the phase angle of the HeNB-*r*-HFANB is substantially lower than that of DeNB-*r*-HFANB even though the swelling is similar. The phase angle is typically larger when PPG or Antifoam is included – as the films did not reach equilibrium prior to the signal from the QCM-D being dampened, the reported phase angles are the minimum values. With the similarity in size between these polyols, the swelling appears to be driven by the PPG component. The reason for the enhanced swelling at ~ 3000 g/mol is likely associated with the nanostructure of the statistical copolymer as χ for the HFANB and the alkyl-NB is expected to be large. Space filling that is defined by the

molecular weight of a polymer additive has been shown to manipulate the free volume of nanocomposites based on grafted nanoparticles.³¹ These effects were explained in terms of the space filling and entropy associated with chain stretching.

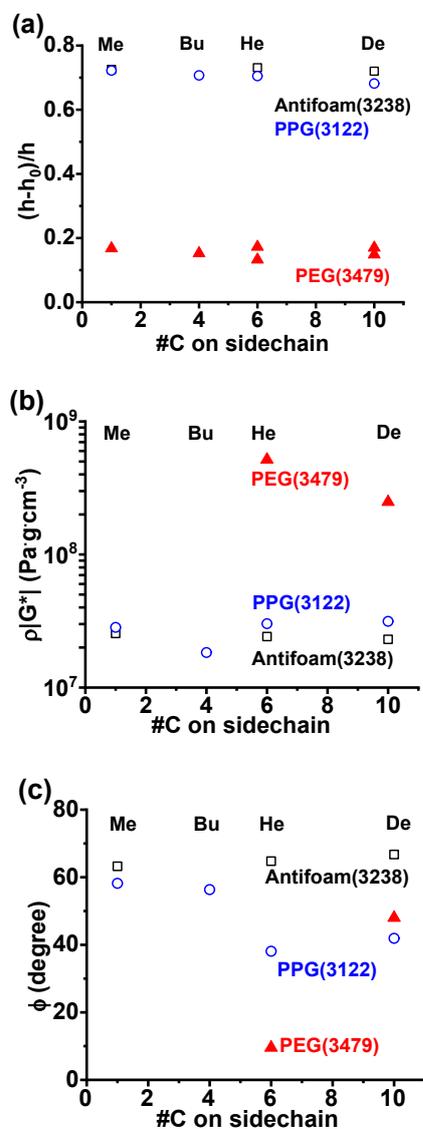


Figure 7. Effect of additive types (PPG/PEG/Antifoam) with similar M_n and sidechain length on the (a) volumetric swelling $[(h-h_0)/h]$, (b) product of the density and magnitude of the complex shear modulus (ρ/G^*) and (c) phase angle (ϕ) for RNB-HFANB (R=Me, He, De) films in 1% butanol with 10ppm additive. Numbers in bracket indicate the M_n . The film thicknesses were MeNB-HFANB ($h_0=344 \pm 84$ nm), BuNB-HFANB ($h_0=261 \pm 5$ nm), HeNB-HFANB ($h_0=290 \pm 25$ nm) and DeNB-HFANB ($h_0=331 \pm 52$ nm)

To further probe the effect of molecular weight and composition for surfactants in the system, the Pluronic series of surfactants were examined as additives. As shown in Figure 8, these surfactants are higher M_n than the Antifoam 204. As expected from the molecular weight dependence of the swelling with PPG (Figure 6), the swelling from these surfactants is less than that from the Antifoam 204.

Interestingly, the swelling observed with Pluronic L121 is less than 40% despite its similarity in molecular weight to PPG ($M_n = 4093$ g/mol) which swells MeNB-r-HFANB by more than 60% (Figure 5a). This substantial difference is unexpected as Pluronic L121 contains 90 wt% PPG, similar to the composition of Antifoam 204 that appears to induce swelling similar to that of PPG ($M_n = 3122$ g/mol). This difference suggests that the hydrophilic ends on the Pluronic surfactants might be important for controlling the swelling in this system. However, PEG-rich surfactants (Pluronic F127 and F108) lead to appreciable swelling in comparison to PEG alone, which illustrates the influence of the PPG on the swelling even when included in a block copolymer with appreciable molecular weight. However, there is limited difference in the swelling with these two surfactants despite the difference in both molecular weight and PPG composition that would lead one to expect lower swelling with the Pluronic F108 based on the swelling with pure PEG and PPG.

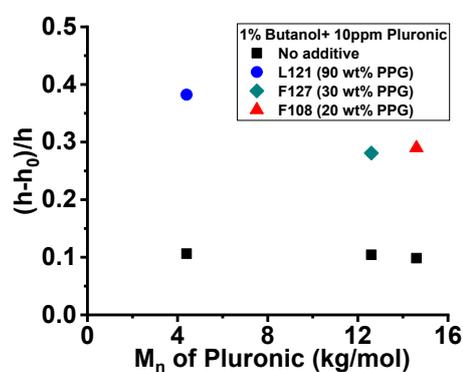


Figure 8. Effect of Pluronic surfactants on the volumetric swelling $[(h-h_0)/h]$ for MeNB-HFANB films ($h_0 = 308 \pm 18$ nm) in 1% butanol with 10ppm additive. Pluronics are block copolymers of PEG-PPG-PEG. The PPG content for each is shown in the legend.

These results illustrate the significance on the molecular weight on the swelling of an amphiphilic copolymer. With the limited differences in the swelling for a systematic series of alkyl side chains for the hydrophobic co-monomer, the swelling appears to be driven by the interaction between the polyol and the hexafluoroisopropanol group, but the more hydrophilic PEG leads to substantially lower overall swelling. The swelling induced by the inclusion of 10 ppm of PPG in the aqueous butanol solution is strongly dependent on molecular weight with a sharp maximum in the swelling when $M_n \approx 3$ kg/mol. This molecular weight effect also appears to be common when considering surfactants based on copolymers of PEG and PPG. These effects suggest a critical size of the polyol to best disrupt the amphiphilic nanostructure of the copolymer to cause substantial swelling (<25 vol% copolymer in the most swollen cases). These effects could be important for a wide variety of amphiphilic polymer membranes, including co-networks, where very dilute oligomers could adversely influence their performance.

Conclusions

In this paper, we have systematically investigated the swelling of amphiphilic copolymer films by aqueous solutions containing small concentrations (10 ppm) of polyols. The alkyl chain length on the hydrophobic comonomer has a limited effect on the swelling in aqueous butanol and even less of an effect when 10 ppm of polyol is present. The inclusion of 10 ppm of PEG to 1 wt% butanol solutions tends to increase the volumetric swelling by approximately 50% with this effect is independent of molecular weight (from ethylene glycol monomer to PEG ($M_n = 3480$ g/mol)). Conversely with PPG, the swelling is molecular weight dependent with the swelling induced by the propylene glycol monomer being similar to that of PEG, while the copolymer film swells to more than 70 vol% solution with 10 ppm PPG (3120 g/mol). At higher molecular weight of PPG, the swelling decreases at the same PPG concentration (10 ppm). This apparent optimal size for the PPG to swell the copolymers is consistent with the size for the common Antifoam 204 that leads to similar swelling. With the same 90 wt% PPG composition on the copolymers, there is a dramatic difference in the swelling induced by Antifoam 204 and Pluronic L121. This difference is qualitatively consistent with expectations for the larger molecular weight of the Pluronic surfactant based on the molecular weight dependent swelling by PPG. These results illustrate the ready incorporation of oligomers into high free volume polymers suitable for membrane separations when there are strong favourable interactions present. The strong sensitivity to the molecular weight of the additive to the swelling of the copolymer is hypothesized to be associated with the molecular size and the structure of the random copolymer, but additional work through systematically tuning the size of the structure of the amphiphilic copolymer (such as with a block copolymer)¹⁶ is needed. Nonetheless, these results provide additional considerations in the design of amphiphilic copolymer membranes for the separation of biologically derived chemicals in terms of oligomeric additives to the fermentation broth that can interact with the membrane and provide potential routes to partially mitigate these effects with the molecular size of the additive.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

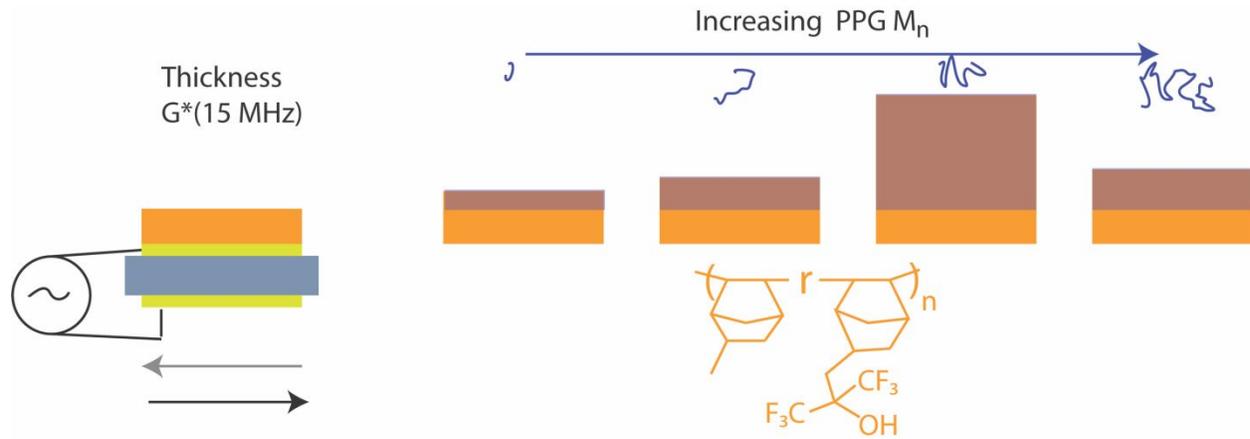
This work was supported by the National Science Foundation under grant no. CMMI-1462284. The authors thank Promerus LLC (Brecksville, OH) for providing the copolymer used in this study and Kazi Sadman for the Matlab code used to fit the QCM-D data to the power-law model. This code is open source and can be downloaded at:

<https://github.com/sadmankazi/QCM-D-Analysis-GUI>.

Notes and references

1. P. Shao and R. Y. M. Huang, *J. Membrane Sci.*, 2007, **287**, 162-179.
2. T. C. Merkel, B. D. Freeman, R. J. Spontak, Z. He, I. Pinnau, P. Meakin and A. J. Hill, *Science*, 2002, **296**, 519-522.
3. W. J. Koros and R. Mahajan, *J. Membrane Sci.* 2000, **175**, 181-196.
4. M. Ulbricht, *Polymer*, 2006, **47**, 2217-2262.
5. H.-J. Huang, S. Ramaswamy, U. W. Tschirner and B. V. Ramarao, *Sep. Purif. Technol.*, 2008, **62**, 1-21.
6. W. S. Guo, H. H. Ngo and J. X. Li, *Bioresour. Technol.*, 2012, **122**, 27-34.
7. N. A. Crowhurst and D. J. Leak, *Int. Sugar J.*, 2010, **112**, 64-73.
8. V. Garcia, J. Pakkila, H. Ojamo, E. Muurinen and R. L. Keiski, *Renewable Sustainable Energy Rev.*, 2011, **15**, 964-980.
9. H. K. S. Panahi, M. Dehghani, J. E. Kinder and T. C. Ezeji, *Biofuel Res. J.*, 2019, **6**, 995-1024.
10. A. Pugazhendhi, T. Mathimani, S. Varjani, E. R. Rene, G. Kumar, S. H. Kim, V. K. Ponnusamy and J. J. Yoon, *Fuel*, 2019, **253**, 637-646.
11. S. P. H. Azambuja and R. Goldbeck, *World J. Microbiol. Biotechnol.*, 2020, **36**, 48.
12. H. Azimi, H. Tezel and J. Thibault, *Chem. Eng. Res. Des.*, 2019, **150**, 49-64.
13. N. Mahmud and K. A. Rosentrater, *Energies*, 2020, **13**, 155.
14. J. Marszalek and W. L. Kaminski, *Chem. Process Eng.*, 2012, **33**, 131-140.
15. S. N. Liu, G. P. Liu, X. H. Zhao and W. Q. Jin, *J. Membrane Sci.*, 2013, **446**, 181-188.
16. D. G. Kim, T. Takigawa, T. Kashino, O. Burtovyy, A. Bell and R. A. Register, *Chem. Mater.*, 2015, **27**, 6791-6801.
17. B. G. Kang, D. G. Kim and R. A. Register, *Macromolecules*, 2018, **51**, 3702-3710.
18. S. Y. Li, M. X. Zhang, E. A. Lewis and B. D. Vogt, *ACS Appl. Polym. Mater.*, 2019, **1**, 3048-3056.
19. G. Guzman, S. M. Bhaway, T. Nugay, B. D. Vogt and M. Cakmak, *Langmuir*, 2017, **33**, 2900-2910.
20. *US Pat.*, 8 214 496, 2009.
21. G. Sauerbrey, *Z. Phys.*, 1959, **155**, 206-222.
22. B. D. Vogt, E. K. Lin, W. L. Wu and C. C. White, *J. Phys. Chem. B*, 2004, **108**, 12685-12690.
23. K. Sadman, C. G. Wiener, R. A. Weiss, C. C. White, K. R. Shull and B. D. Vogt, *Anal. Chem.*, 2018, **90**, 4079-4088.
24. G. C. DeNolf, L. F. Sturdy and K. R. Shull, *Langmuir*, 2014, **30**, 9731-9740.
25. E. J. Martin, M. T. Mathew and K. R. Shull, *Langmuir*, 2015, **31**, 4008-4017.
26. G. E. dePolo, E. Schafer, K. Sadman, J. Rivnay and K. R. Shull, *J. Visualized Exp* 2020, DOI: 10.3791/60584.
27. D. E. Delgado, L. F. Sturdy, C. W. Burkhart and K. R. Shull, *J. Polym. Sci. Part B: Polym. Phys.*, 2019, **57**, 1246-1254.
28. M. V. Voinova, M. Rodahl, M. Jonson and B. Kasemo, *Phys. Scr.*, 1999, **59**, 391.
29. U. Zettl, A. Knoll and L. Tsarkova, *Langmuir*, 2010, **26**, 6610-6617.
30. X. X. Li and B. D. Vogt, *Polymer*, 2009, **50**, 4182-4188.
31. C. R. Bilchak, E. Buenning, M. Asai, K. Zhang, C. J. Durning, S. K. Kumar, Y. Huang, B. C. Benicewicz, D. W. Gidley and S. Cheng, *Macromolecules*, 2017, **50**, 7111-7120.

Table of Contents Entry



Not too big, not too small, but a narrow molecular weight range for poly(propylene glycol) where swelling of the copolymer increases tremendously for poly(propylene glycol).