

Detailed Compositional and Structure–Property Analysis of Ethylene Oxide-Propylene Oxide Triblock Copolymers

Gergő Róth, Tibor Nagy, Ákos Kuki, Levente Novák, Dávid Nyul, Miklós Zsuga, and Sándor Kéki*

The polyethylene oxide-polypropylene oxide (PEO-PPO) based triblock copolymers are notable amphiphilic copolymers with a diverse range of applications. The presence of homo-, and/or diblock impurities in copolymers with PEO-PPO-PEO triblock has been demonstrated. This finding suggests that the samples are blends rather than pure triblock copolymers. Furthermore, copolymers with triblock copolymer content of 0 or less than 20% by molar percentage have been identified. The hydrophilic-lipophilic balance (HLB) is also calculated based on the exact composition of the blends. The effect of HLB values and compositional data on the initial foam height (in casein solution), the surface tension, and the contact angle are investigated. The correlation coefficients for the PPO-PEO-PPO copolymers versus HLB values are found to be high, while those obtained for the PEO-PPO-PEO copolymers versus values of HLB are significantly lower. The lower correlation coefficients for the PEO-PPO-PEO samples can be attributed to the presence of homo- and diblock (co)polymer contaminants. In addition, a linear regression model has been constructed to find a mathematical relationship between the percentage of ethylene oxide, the average number of propylene oxide units, and the properties of the copolymer.

1. Introduction

The polyethylene oxide – polypropylene oxide (PEO-PPO) based block copolymers are amphiphilic block copolymers with a considerable number of potential applications.^[1–4] This extensive range is derived from their diversity in size and composition, which allows the tuning of the (co)polymer characteristics.^[5]

In these amphiphilic block copolymers (also called poloxamers), the hydrophilic PEO and hydrophobic PPO blocks can be arranged to yield PEO-PPO-PEO or reversed PPO-PEO-PPO triblock sequence. The different types of triblock copolymers have diverse applications, but all types have both hydrophobic and hydrophilic segments, which can form micelles in certain solvents and appropriate surface active properties utilized in various foam controlling, anti-, or defoaming applications in the paper industry, water treatment, sugar beet processing, fermentation, machine

dishwashing, and so on.^[6–9] The diversity and multifunctionality of these copolymers are also demonstrated by their potential medical application such as nanocarriers for drug delivery systems.^[5,6,8–12]

To address the increasing demand for such polymers and to involve green chemistry principles, the efficiency of these block copolymers should be improved. One method is to improve their performance as surfactants by optimizing their structure. The surfactants can be classified based on their hydrophilic-lipophilic balance (HLB) values, which are directly related to their chemical structure.

The HLB value was introduced by Griffin.^[13] Since then the HLB values have been used to find tendencies in different surfactant characters. Later, Griffin suggested further methods to define the HLB value of nonionic surfactants and their mixtures.^[14] However, some block polymer chains such as polypropylene oxide and polybutylene oxide reveal behaviors that are not only related to their structure.^[13] Davis proposed a calculation of the HLB value based on a functional group contribution,^[15] but due to the non-linear nature of the hydrophilicity of PEO block size, the development of further model is required. Guo et al. used a two-parameter gamma probability distribution function to determine the effective chain length of PEO.^[16] In addition, two simple empirical equations were

G. Róth, T. Nagy, Á. Kuki, D. Nyul, M. Zsuga, S. Kéki
 Department of Applied Chemistry
 Faculty of Science and Technology
 University of Debrecen
 Egyetem tér 1, Debrecen H-4032, Hungary
 E-mail: keki.sandor@science.unideb.hu

L. Novák
 Department of Physical Chemistry
 Faculty of Science and Technology
 University of Debrecen
 Egyetem tér 1, Debrecen H-4032, Hungary
 D. Nyul
 Doctoral School of Chemistry
 University of Debrecen
 Egyetem tér 1, Debrecen H-4032, Hungary

 The ORCID identification number(s) for the author(s) of this article can be found under <https://doi.org/10.1002/mame.202400297>

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proposed for two cases when $n^{\text{EO}} < 50$ and $n^{\text{EO}} > 50$, where n^{EO} is the average number of ethylene oxide units in a PEO block.

Furthermore, the knowledge of the HLB-property or structure-property relationship allows one to optimize the properties and find better alternatives for certain applications. However, the structural analysis is not a straightforward task due to the complexity and diversity of the copolymers.^[17,18] Although there are several methods available for the characterization of copolymers, most of them provide only the average properties.^[19] Recently, we have developed a mass spectrometry-based method for the detailed analysis of copolymers.^[20–22] To prove the efficiency of our method, PEO-PPO triblock copolymer samples were analyzed as model polymers. We have observed differences in the copolymer composition and size between the expected (provided by the manufacturer) and measured values. In addition, polymeric impurities were identified in these samples. It was demonstrated that a detailed analysis allowed us to understand the behavior of these copolymers under size exclusion chromatography (SEC) conditions and artificial neural networks were developed to translate the SEC behavior into structural information.^[23]

In this article, we report the determination of chemical composition and number-average molecular weight of twenty-five different PEO-PPO triblock copolymers. Using the results of the detailed characterizations (chemical composition, HLB), we also investigated the relationships between the copolymer characteristics and their antifoaming properties, such as the initial foam height, the surface tension, and the contact angle (hydrophobized glass). In addition, we developed a simple linear model to estimate the properties of the polymer with the knowledge of the exact sample composition.

2. Results and Discussion

2.1. Analysis of the Copolymers

Triblock copolymers built from ethylene oxide (EO) and propylene oxide (PO) monomers have two possible structures, the PEO-PPO-PEO sequence is known as the normal structure and the PPO-PEO-PPO sequence is called the reverse structure. Both are important copolymers. Although these polymers are produced in large quantities worldwide, in many cases their behavior is not well understood. The most common challenge arises from the inherent complexity of the copolymers, which makes it very difficult to determine the exact structure-property relationships. Recently, we have developed mass spectrometry-based methods for the detailed characterization of copolymers, allowing the identification of the number of monomer units and even their distribution in the copolymer.^[24,25] The methods were validated through the use of ^1H -NMR and size exclusion chromatography (SEC) measurements. **Table 1** summarizes the copolymer characteristics determined by our methods, including the number average molecular weight (M_n), the weight fraction (EO%) of the ethylene oxide units, the number-average and the weight-average number of the EO and PO units (n_n^{EO} , n_n^{PO} , n_w^{EO} , n_w^{PO}) and the percentage of the primary hydroxyl end-groups.^[24] In addition, the expected copolymer characteristics (composition, molecular weight, and HLB value) are given from the literature.^[3,26]

Table 1 shows that there are only slight differences in many cases between the EO fraction (EO%) and the number average molecular weight published in the literature and determined by our methodology. However, there are some samples where significant differences were observed. For instance, sample 31R1 was found to contain 18% EO by weight, in contrast to the expected 10%. The M_n of this polymer is similar to the expected, which also implies a shorter chain length for the PPO block. Furthermore, additional discrepancies were identified for the samples PE6200 and PE84. The PE6200 appears to be a PE6300 copolymer based on the measured M_n and EO content, as the EO% is 31%, whereas the M_n is 2510 g mol^{-1} . Higher molecular weight Pluronic samples may contain impurities that result in a bimodal distribution as was observed for the sample PE84 (Figure S26, Supporting Information). Batsberg et al. conducted the separation of the fractions present in Pluronic samples. They found that the presence of lower levels of impurities resulted in minor alterations in composition and micellization between the bulk and the fractions.^[27] However, it is important to note that these samples are blends rather than pure copolymers. The M_n of the main series is considerably different, 5060 and 3750 g mol^{-1} have been found for the measured and the expected values, respectively.

To gain deeper insight into the structural diversity, we determined the percentage of the primary hydroxyl end groups using ^1H -NMR, and the results of this investigation are presented in **Table 1**. In line with the typical PEO-PPO-PEO triblock sequence, secondary hydroxyl end-groups are not expected since both terminal blocks are PEO chains. However, all PEO-PPO-PEO triblock copolymer samples showed primary hydroxyl end-group percentages below 100%. Furthermore, some of these PEO-PPO-PEO triblock copolymers exhibit primary hydroxyl end-group percentages below 50%, indicating the presence of not only diblock impurities but also PPO homopolymers. These homopolymer series were also detected by MALDI-TOF mass spectrometry. As an example, the mass spectrum and the identified homopolymer series of the PE8100 are presented in the (Figure S27, Supporting Information).

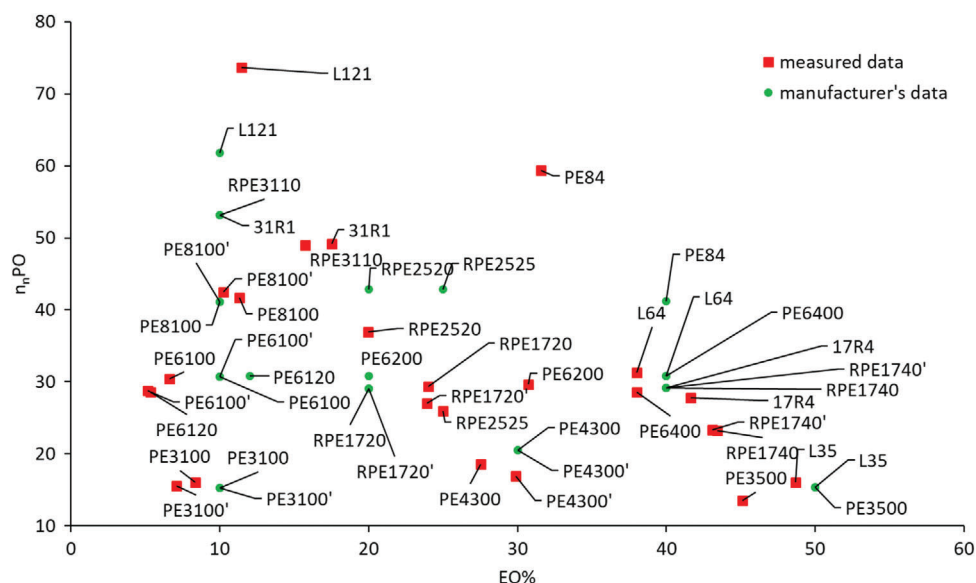
Figure 1 shows a comparison between the n_n^{PO} and EO% of the investigated copolymers, based on literature data and our expected values, although no clear trend could be identified. For copolymers with low EO content, the measured EO% is consistently lower than expected for PEO-PPO-PEO copolymers. Conversely, for the PPO-PEO-PPO copolymers, the EO% is consistently higher than expected. Notably, significant differences in EO content were observed low EO%, range. The copolymers investigated in this study included several analogue pairs, such as the RPE1740-17R4, and PE3500-L35 copolymers. Despite having theoretically similar composition and molecular weight, differences were found between them. These findings highlight the importance of a comprehensive analysis of these copolymers.

2.2. Calculation and Use of HLB Value for Structure–Property Relationships Analysis

The hydrophilic-lipophilic balance (HLB) is applied as a common characteristic of surfactants. It is noteworthy that a considerable number of publications employ the HLB values as defined by the manufacturer, despite the lack of clarity

Name	EO% [*]	$n_n^{\text{PO}*}$	HLB [*]	EO% (MS)	M _n (MS)	n_n^{PO}	n_w^{PO}	n_n^{EO}	n_w^{EO}	primary OH end %	HLB ^a
L35	50	15.4	19	49	1840	16.0	16.4	20.4	24.6	90.4	20.3
17R4	40	29.1	12	42	2800	27.8	28.4	26.4	27.0	0.0	10.2
L64	40	30.8	15	38	2960	31.3	31.7	25.5	28.4	91.8	19.0
PE84	40	41.2	14	32	5060	59.4	61.3	36.3	38.3	92.4	12.9
L121	10	61.8	1	11	4850	73.7	74.0	12.5	15.4	78.3	0.3
31R1	10	53.2	1	18	3480	49.2	49.7	13.8	14.3	0.0	1.4
RPE1720'	20	29.1	6	24	2080	27.0	27.7	11.3	12.0	9.0	7.5
PE3500	50	15.4	19	45	1460	13.5	14.9	14.9	20.7	83.5	20.3
RPE1740'	40	29.1	12	43	2410	23.3	23.8	23.6	24.1	0.0	11.2
PE4300'	30	20.5	12	30	1420	16.9	18.0	9.6	13.8	76.5	15.7
RPE2525	25	42.9		25	2030	25.9	26.5	11.5	12.1	5.2	7.9
PE3100'	10	15.2	5	7	990	15.5	16.1	1.6	3.8	28.8	0.5
PE6100'	10	30.8	3	5	1780	28.8	29.7	2.1	4.6	43.2	-1.3
PE8100'	10	41.1	2	10	2760	42.4	43.0	6.4	9.1	64.3	4.3
PE6120	12	30.8		5	1770	28.6	29.7	2.1	4.6	42.2	-1.0
PE6400	40	30.8	15	38	2710	28.6	29.0	23.3	27.0	92.1	19.2
PE3100	10	15.2	5	8	1040	16.1	16.5	2.0	4.3	32.3	2.2
PE4300	30	20.5	12	28	1510	18.5	19.0	9.4	13.4	79.4	15.0
PE6100	10	30.8	3	7	1910	30.4	31.1	2.8	5.3	46.8	1.0
RPE1720	20	29.1	6	24	2260	29.3	30.0	12.3	13.1	0.0	7.1
PE6200	20	30.8	7	31	2510	29.7	30.1	17.5	19.9	86.6	16.6
PE8100	10	41.1	2	11	2750	41.7	42.2	7.0	9.7	69.7	5.4
RPE1740	40	29.1	12	43	2410	23.2	23.6	23.8	24.2	0.0	11.3
RPE2520	20	42.9	4	20	2700	37.0	37.5	12.2	12.8	0.0	4.7
RPE3110	10	53.2	1	16	3390	49.0	49.5	12.1	12.8	0.0	1.0

Figure 1. The average number of the PO units versus EO% is based on the literature data (green-filled circle) and our measurements (red-filled rectangle).



surrounding the methodology used in its calculation. Consequently, it is not feasible to adopt directly the methodology and the identified structural data. To overcome this issue, Kozolov proposed an empirical equation to define the HLB values of Pluronics derived from BASF.^[26] The evaluation of the structure-property relationships or the use of HLB values is limited due to the significant compositional differences between the literature and the measured data, resulting in an unexpectedly high deviation. Accordingly, we utilized a slightly modified version of the effective chain length (ECL) method for the HLB calculation,^[16] wherein only minor modifications were required, as detailed in the Supporting Information. The calculated HLB values are summarized in Table 1. To gain further insight into the behavior of these block copolymers, we investigated the relationships between the HLB values and the antifoaming properties, such as initial foam height, surface tension, and contact angle of copolymer solutions (Figure 2). The measured data and further details can be found in the, Table S2–S8 (Supporting Information).

For the calculation of the HLB values, the effective length of both the PEO and PPO blocks is taken into account, however, the molecular weights and the absolute length of the blocks are not considered. As depicted in Figure 2, the normal (PEO-PPO-PEO) and the reverse (PPO-PEO-PPO) block copolymers were investigated separately. The Pearson's correlation coefficients between the HLB and initial foam height, surface tension, and contact angle for the reverse copolymers are $r_{\text{initial foam height}}$: 0.960, $r_{\text{surface tension}}$: 0.955, and $r_{\text{contact angle}}$: 0.746, respectively. The high correlations demonstrate that the HLB values significantly influenced the investigated properties. Based on the HLB values, these parameters can be predicted. In contrast, the copolymers with PEO-PPO-PEO sequence reveal low or no correlation at all. This finding may be attributed to the presence of various polymeric species in the polymer samples as previously demonstrated. The high deviation may have originated from the simultaneous presence of homopolymers, diblock, and triblock copolymers, which influence the HLB values. For example, the PE8100 copolymers (of which there are two analogs, PE8100 and PE8100') consisting of homo, di- and triblock copolymers exhibit low EO content and a low percentage of primary hydroxyl end-groups. These samples show excellent antifoaming activity. Moreover, samples with comparable composition, but differing in PPO block lengths (PE3100 and L121) reveal diminished antifoaming activity. Interestingly, the decrease of the height of the foam upon the effect of an antifoaming agent, i.e., in the presence of triblock copolymers in our case, can be described by an exponential decay function (Equation S5, Supporting Information). Representative examples for the fitted relative height of the foam versus time curves can be found in the Supporting Information together with the relationship between the relative height and time (Figure S28, Supporting Information). Another factor could be the presence of a small amount of PPO homopolymers and diblock copolymer impurities, as estimated from the percentage of primary hydroxyl ends. These impurities result from the reactivity difference between primary and secondary hydroxyl ends during copolymer synthesis. For copolymers with reverse structures, good correlations were found between HLB values, surface tension, and contact angle. For the PEO-PPO-PEO triblock copolymers low correlation coefficients were ob-

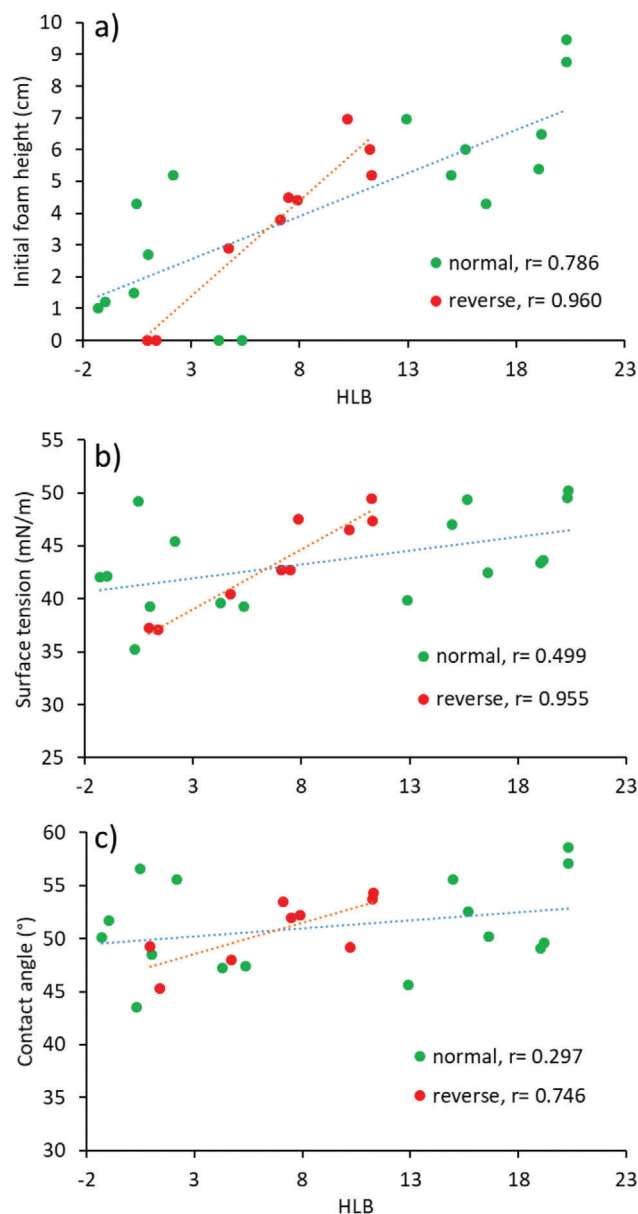


Figure 2. The initial foam height (a), the surface tension (b) and the contact angle (c) as a function of HLB values. The PEO-PPO-PEO triblock copolymers (normal) are shown in green, while the reverse copolymers (PPO-PEO-PPO) are shown as red dots. The r values represent Pearson's correlation coefficients. The concentrations of the copolymer solutions were 0.1 g L^{-1} , $c_{\text{caseinate}}$: $0.5 \text{ w/w\%}$.

tained, in line with the initial foam height (antifoaming activity). These low values originated from the small effect of HLB on the surface tension and contact angle and from the high deviation of the values due to the structural inhomogeneity as discussed previously.

In order to gain deeper insight into the relationship between the structure and properties, the compositions of the copolymer samples were calculated through a comprehensive structural analysis. The homopolymer content is available from the mass spectrometric analysis, whereas the primary and secondary

Table 2. The percentage of primary hydroxyl end groups, the percentage of homopolymer content, and the calculated di- and triblock content. The end groups were identified by $^1\text{H-NMR}$ while the homopolymer content was determined by mass spectrometry.

Sample name	Primary ends [%]	Homopolymer content [%]	Diblock content [%]	Triblock content [%]
L35	90.4	2.1	15.0	83.0
L64	91.8	0.2	16.0	83.8
PE84	92.4	0.0	15.3	84.7
L121	78.3	0.2	43.1	56.8
PE3500	83.5	3.3	26.3	70.4
PE4300	76.5	6.4	34.1	59.5
PE3100	28.8	40.5	59.5	0.0
PE6100	43.3	34.9	43.7	21.4
PE8100	64.3	8.4	54.5	37.0
PE6120	42.2	34.7	46.2	19.0
PE6400	92.1	0.8	14.3	85.0
PE3100	32.3	34.7	65.3	0.0
PE4300	79.4	7.1	27.2	65.8
PE6100	46.8	25.4	55.5	19.0
PE6200	86.6	0.0	26.8	73.2
PE8100	69.7	6.5	47.5	46.0

hydroxyl ends were determined by $^1\text{H-NMR}$. In this study, we assumed that all secondary hydroxyl groups originated from PPO chain ends. However, it is possible that a small fraction of primary hydroxyl end-groups may be present in a PPO homopolymer. As previously demonstrated, the presence of primary end-groups in PPO homopolymers is below 2%.^[28] Table 2 provides a detailed account of the percentage of primary hydroxyl end-groups and the homopolymer content as well as the calculated diblock and triblock content of the PEO-PPO-PEO copolymers as determined by $^1\text{H-NMR}$ and mass spectrometry.

Table 2 demonstrates that all samples contain at least two distinct polymer series, indicating that the samples are complex polymer blends and not pure triblock copolymers. In the case of the PE3100 sample, which consists exclusively of homopolymer and diblock copolymer, the triblock structure is completely missing. As the EO content in the samples increases, the presence of homopolymers decreases, and diblock copolymers become the

dominant species. The composition of the blends is highly dependent on the EO%. Blends with 40% or 50% EO content reach a maximum triblock content of $\approx 84\%$ among the samples investigated. The number of EO units (n_{EO}) is closely related to the composition of the blends. A relationship, described by a saturation curve (Equation 1), has been established between the percentage of the primary hydroxyl end-groups and the n_{EO} .

$$\text{Primary OH\%} = A \left(1 - e^{-\frac{n_{\text{EO}}}{B}} \right) \quad (1)$$

where PrimaryOH% is the percentage of the primary hydroxyl end groups determined by $^1\text{H-NMR}$, n_{EO} is the average number of EO units, and A and B are constants ($A = 90.26$; $B = 4.74$).

The results of the fitting and the parity plot are shown in Figure 3. As seen in Figure 3, the curve calculated by Equation (1) fits very well with the experimental data.

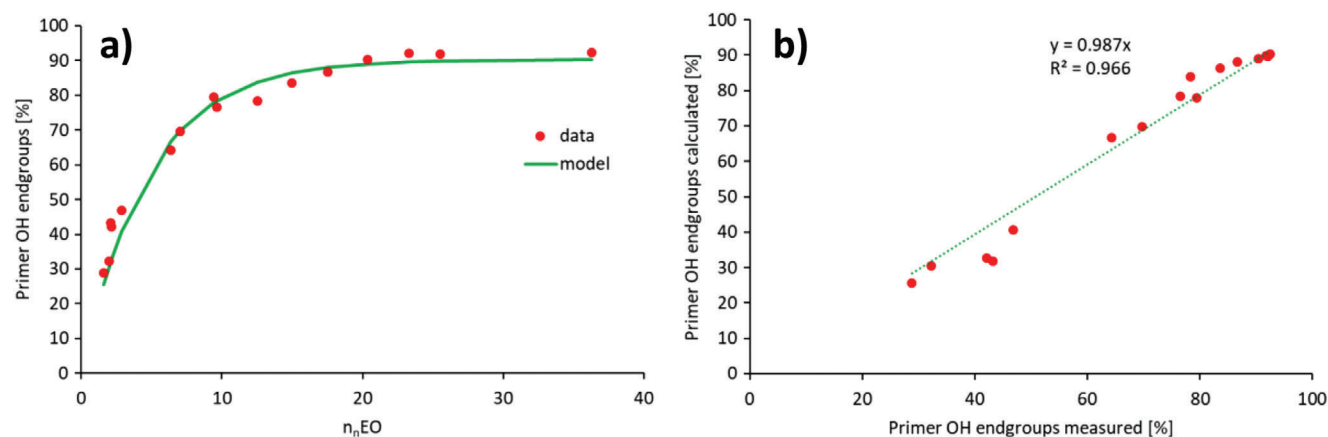


Figure 3. a) The primary hydroxyl end groups versus the n_{EO} , (model is a saturation curve, Equation 1); b) the parity plot of the fitting.

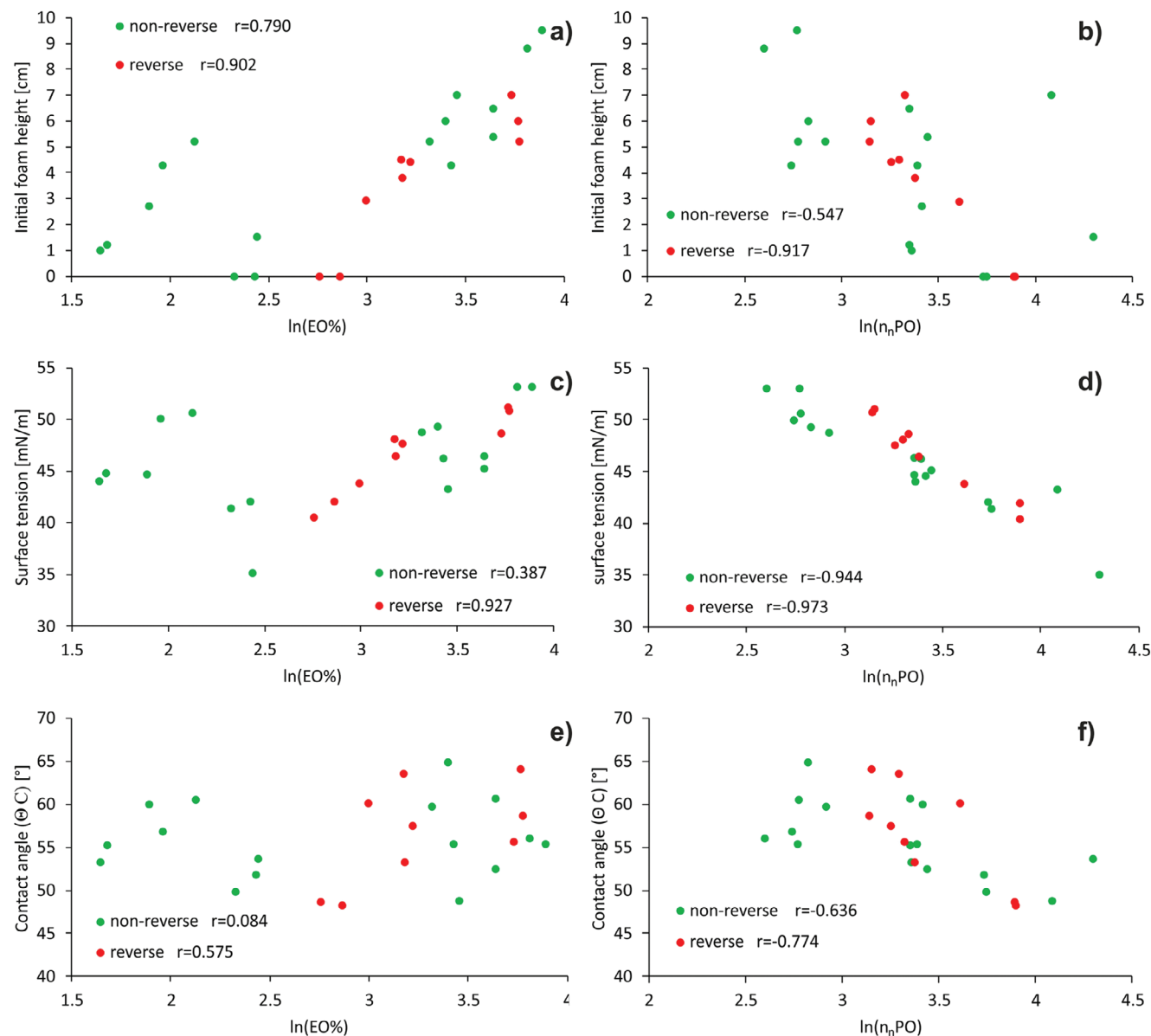


Figure 4. The initial foam height (a,b), the surface tension (c,d), and the contact angle (e,f) as a function of $\ln(\text{EO}\%)$ and $\ln(n_n\text{PO})$. The PEO-PPO-PEO triblock copolymers are shown in green, while the reverse copolymers are shown as red dots. The r values represent the Pearson's correlation coefficients. The concentrations of the copolymer solutions were 0.1 g L^{-1} , $c_{\text{caseinate}}: 0.5 \text{ w/w}\%$.

The composition of the blends (samples) with a PEO-PPO-PEO sequence allows a more precise calculation of the HLB values, which can be used to identify the structure-property relationships more precisely. The HLB values were calculated for the di- and triblock copolymers individually, and subsequently weighted according to their respective percentages. The homopolymers were excluded from further analysis. Better Pearson's correlations between the investigated properties and the HLB values were found when the homo and diblock contents were included in the calculation. The correlation coefficients obtained are $r_{\text{initial foam height}}: 0.832$, $r_{\text{surface tension}}: 0.571$ and $r_{\text{contact angle}}: 0.376$. These values and the figures can be found in the Figure S29 (Supporting Information). In summary, our results demonstrate that

the HLB concept is a simple and effective tool for describing the properties of surfactants. However, block copolymers may exhibit unique effects that are not directly related to their structure.^[13]

2.3. The Use of Chemical Compositional for Structure-Property Relationships Analysis

The use of the HLB values yielded constrained efficiency, promoting an investigation into polymer antifoaming properties correlated directly with composition. Initially, the influence of EO% and PO% on the polymer properties was investigated. It was observed that the $\ln(n_n\text{PO})$ exhibited a higher correlation than

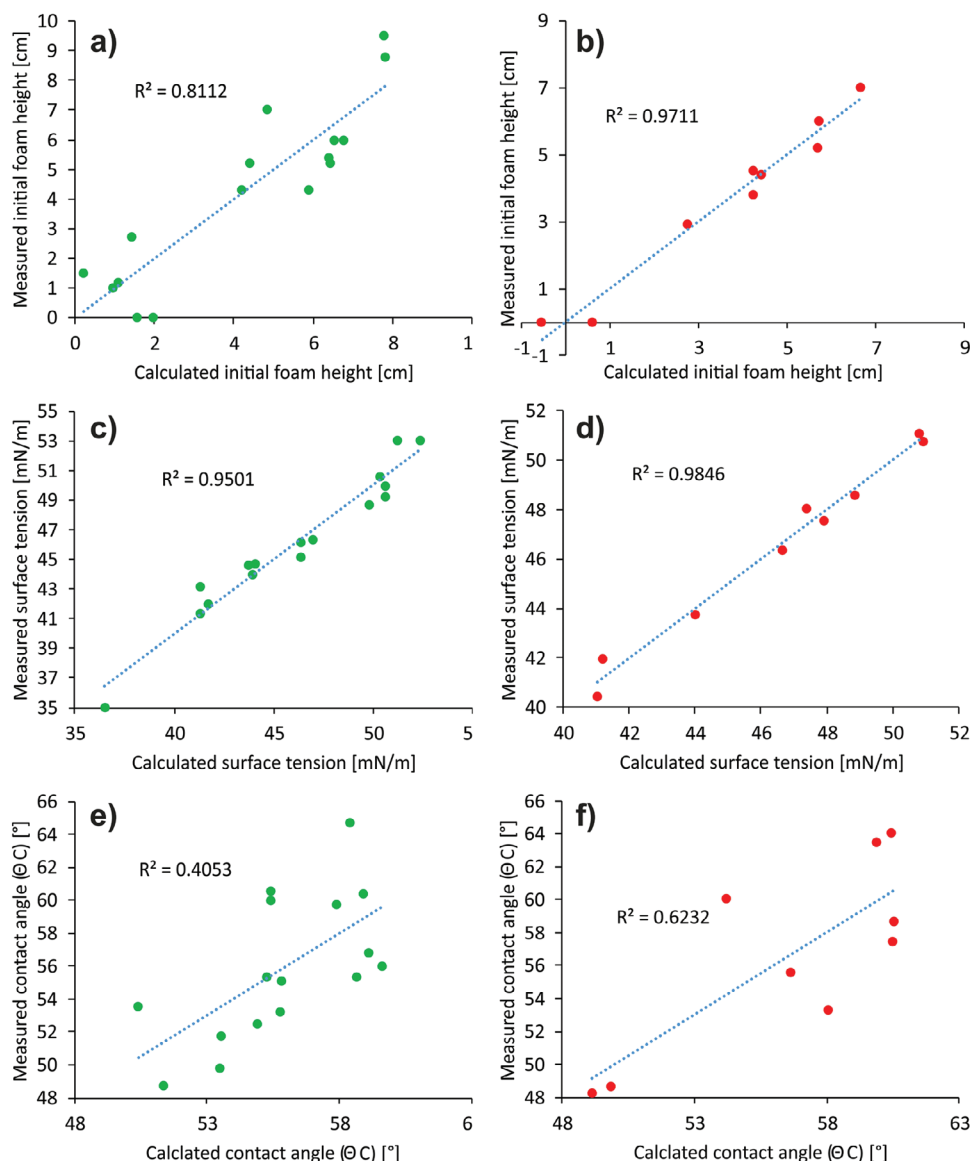


Figure 5. Parity plots between the experimentally obtained and calculated data by our linear model for the initial foam height (a,b), surface tension (c,d), and contact angle (e,f). The PEO-PPO-PEO copolymers are indicated by green, while the reverse PPO-PEO-PPO copolymers are represented by red dots.

the use of PO%. This is consistent with the hypothesis that the properties are influenced by the length of the PPO chain, rather than by the PO%. Significant correlations were found between the $\ln(n_{\text{n}}^{\text{PO}})$ and the initial foam height, surface tension, and contact angle as demonstrated in **Figure 4**.

As was previously observed, the copolymers with a reverse structure yielded excellent correlation coefficients in all cases. The initial foam height was found to be strongly dependent on the $\ln(\text{EO}\%)$ (positive) and $\ln(n_{\text{n}}^{\text{PO}})$ (negative) for the PPO-PEO-PPO triblock copolymers, whereas for PEO-PPO-PEO triblock copolymers a strong correlation was observed only for the $\ln(\text{EO}\%)$ (positive). These findings demonstrate that the antifoaming activity increases with the length of the PPO chains, while the EO content has an antifoaming weakening effect. For the PEO-PPO-PEO triblock copolymers, a similar trend was ob-

served, however, the correlation is weaker. Upon analyzing the surface tension, strong correlations were found with the exception of the correlation between the $\ln(\text{EO}\%)$ and surface tension for the PEO-PPO-PEO triblock copolymers. Based on the correlation coefficients, it can be concluded that the compositional evaluation is a more effective method than using the HLB values.

In order to obtain a more detailed description of the impact of composition on the properties, linear models have been developed that incorporate the combined effect of the $\text{EO}\%$ and n_{n}^{PO} (Equation 2)

$$y = \alpha \times \ln(n_{\text{n}}^{\text{PO}}) + \beta \times \ln(\text{EO}\%) + \gamma \\ \times \ln(n_{\text{n}}^{\text{PO}}) \times \ln(\text{EO}\%) + \delta \quad (2)$$

Table 3. The parameters of the linear regression models were obtained for the PEO-PPO-PEO and PPO-PEO-PPO triblock copolymers, respectively. The R^2 values derived from the parity plots are also included.

Initial foam height	α	β	γ	δ	R^2
PEO-PPO-PEO	-6.78536	-2.24896	1.499014	19.16608	0.81
PPO-PEO-PPO	-36.5083	-33.4478	11.37736	111.7147	0.97
Surface tension	α	β	γ	δ	R^2
PEO-PPO-PEO	-13.4716	-4.3751	1.754014	86.69476	0.95
PPO-PEO-PPO	-2.73451	10.00424	-2.06489	46.23595	0.98
Contact angle	α	β	γ	δ	R^2
PEO-PPO-PEO	-5.41371	-0.02435	-0.05472	74.32037	0.41
PPO-PEO-PPO	-12.7356	4.040662	-2.61386	116.3362	0.62

where n_n^{PO} is the average number of PO units, EO% is the weight percentage of the EO in the samples y is the initial foam height or surface tension or contact angle, α , β , γ and δ are constants.

The fitted models demonstrate efficiency in elucidating the structural dependence of the initial foam height, surface tension, and contact angle. The parity plots of the models are presented in Figure 5. The models provide high R^2 values with the exception of the contact angle. The parameters of the linear regression models are summarized in Table 3. These high R^2 values, in comparison to the single factor dependence and the parameters c , indicate that there is a significant interaction between the n_n^{PO} and EO% with respect to the initial foam height and surface tension. On the contrary, the R^2 values are small for the edge angle, indicating that the contact angle does not vary significantly with the composition. This is consistent with the observation that all polymers exhibit similar wetting properties, as noted also in the single-factor analysis.

3. Conclusion

In this paper, we reported a detailed analysis of 25 PEO-PPO triblock copolymers. The analysis covered copolymers with both the normal (PEO-PPO-PEO) and reverse (PPO-PEO-PPO) sequences. First, we carried out a comprehensive mass spectrometric analysis of the copolymers, which yielded the number average molecular weight (M_n), the weight fraction (EO%) of the ethylene oxide units, the number-average and the weight-average number of the EO and PO units (n_n^{EO} , n_n^{PO} , n_w^{EO} , n_w^{PO}). Furthermore, the percentages of the primary hydroxyl end groups were determined by ^1H -NMR. The investigation of the quality of the end groups revealed a low primary hydroxyl end-group content for the PEO-PPO-PEO copolymers. According to their symmetric nature, it is reasonable to conclude that only primary hydroxyl end-groups would be present at the chain-ends. However, in numerous instances, the aforementioned value was less than 50 percent. This demonstrates the presence of not only diblock copolymers but also homopolymers. In some cases, the triblock copolymer content was found to be very low, 0 or less than 20%.

In order to gain deeper insight into the relationships between the composition and the properties of copolymer solutions such as the initial foam height (in casein solution), surface tension, and contact angle, the impact of the composition on these properties was also investigated.

High Person's correlation coefficients were obtained for the reverse copolymers. In contrast, the correlation coefficients for the PEO-PPO-PEO copolymers showed weaker correlations between the HLB and the properties of copolymer solutions. The HLB values were calculated based on the ratio of the hydrophilic and lipophilic blocks, and thus the length of the chains was not involved in these calculations. Accordingly, the average number of PO units and the percentage of EO content were employed in further analysis of the polymer solutions. Linear regression models involving the interaction between the average number of PO units and the percentage of EO content were developed. The measured and fitted data demonstrated a high level of correlation.

The results highlight the complexity of PEO-PPO-PEO triblock copolymers, and therefore a more detailed analysis is recommended to elucidate the structure-property relationship.

4. Experimental Section

Chemicals: Copolymers produced by BASF were generous gifts (Ludwigshafen, Germany). Additional copolymers, indicated by ' were received in 2006, while the others were obtained in 2021. Further copolymers were purchased from Merck (Darmstadt, Germany). Water was purified by a Direct-Q water system (Millipore, Molsheim, France). Casein sodium salt from bovine milk and EtOH was purchased from Merck (Darmstadt, Germany). All other chemicals used were of analytical grade.

Matrix-Assisted Laser Desorption/Ionization Time-of-Flight Mass Spectrometry (MALDI-TOF MS): The measurements were carried out by an Autoflex Speed MALDI-TOF MS instrument (Bruker Daltonik, Bremen, Germany) instrument. Reflectron mode was applied, the ion source voltage 1, ion source voltage 2, reflector voltage 1, and reflector voltage 2 were 19, 16.65, 21, and 9.55 kV, respectively. The mass spectrometer was equipped with a solid-phase laser (355 nm). External calibration was applied using polyethylene glycol and polypropylene glycol homopolymers. The *trans*-2-[3-(4-*tert*-Butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) matrix and sodium trifluoroacetate (NaTFA) ionizing agent dissolved in methanol were used for sample preparation. The concentrations of the matrix, samples, and ionizing agents were 20, 10, and 5 mg mL⁻¹, respectively, while the mixing ratio was 25:2:1. 0.5 μ L mixture was deposited on the surface of the MALDI plate and allowed to air-dry.

Initial Foam Height: The initial foam height was measured according to the ASTM D1173 standard. The temperature was 49 °C and the Caseinate solution was 0.5 w/w%. The pH of the Caseinate solution was 8, which was adjusted by Britton-Robinson buffer (BRB). The Caseinate solution was prepared in BRB solution and was stirred at room temperature for 24 h. The copolymers were dissolved in EtOH of 1 mL added to the Caseinate solution and vigorously stirred and heated before the measurement. The copolymer concentrations were 0.1, 0.05 and 0.01 g L⁻¹. The error of the measurements was determined by replicates of blank solutions, the RSD% was found to be 2.95%.

Contact Angle: Contact angles were determined on a glass surface, hydrophobized by trimethylsilyl chloride. In every case, 5 μ L solutions were dropped on the glass. The solution was prepared with purified water, the concentrations of the polymers were 0.1 and 0.75 g L⁻¹. All measurements were repeated three times, and the average of the contact angle of fitted circles (θ_C) was used. The error was calculated based on the replicates, the average of the RSD% was 2.3%.

Surface Tension: The measurements of the surface tensions were carried out with a du Noüy type Krüss tensiometer (Hamburg, Germany), at 25 °C. The concentrations of the solvents were 0.1 and 0.75 g L⁻¹. The tensiometer was calibrated with purified water. The platinum ring was heated before each measurement. The samples were measured five times, and the

corrected average values were used. The average RSD% of the replicates was 0.42%.

Nuclear Magnetic Resonance Spectroscopy (NMR): The NMR experiments were carried out using a Bruker Avance II 500 MHz spectrometer. The instrument was equipped with a 5 mm z-gradient TXI probe (Bruker Daltonik, Bremen Germany). The primary and secondary hydroxyl functions were determined by $1D-^1H$ NMR experiments at 300 K with a single scan, a 90-degree ^1H excitation pulse with a spectral width of 14.97 ppm (32 768 data points). An exponential window function with 0.3 Hz line broadening was applied to the time data prior to the Fourier transform. The spectra were evaluated by the Bruker TopSpin computer software (version 2.1 and 4.1). The samples were dissolved in $CDCl_3$ (30 mg/600 μ L) and a tenfold molar excess of trifluoroacetic anhydride was added. The solutions were maintained at room temperature for 20 h prior to analysis. The primary and the secondary hydroxyl group contents were calculated using the integrals of proton signals at 4.5 ppm and, 5.2 ppm, respectively. The integrals are summarized in the Table S1 (Supporting Information). The ^1H NMR spectra are shown in the Supporting Information (Figures S1–S25, Supporting Information).

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords

detailed copolymer analysis, diblock impurity, initial foam height, PEO-PPO block copolymers, poloxamers

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