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Study of interfacial tension in poly(ethylene oxide)/polystyrene/diblock copolymer system by electric deformation method

Satoru Moriya[1], Syota Kawamoto[2], Osamu Urakawa, Keiichiro Adachi*

Department of Macromolecular Science, Graduate School of Science, Osaka University, 1-1 Machikaneyama, Toyonaka, Osaka 560-0043, Japan

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Abstract

We investigated the interfacial tension γ between poly(ethylene oxide) (PEO) and polystyrene (PS) focusing our attention on the dependence of γ on the molecular weight (M) of PEO and the surfactant effect of poly(ethylene oxide-*b*-styrene) diblock copolymer [P(EO-*b*-S)]. Measurements of γ were carried out by observing electric deformation of droplets of PEO suspended in bulk PS or in a concentrated solution of PS in dioctylphthalate (DOP). The results indicate that γ between PEO and PS is almost independent of M of PEO in the high molecular weight region, but exhibits a minimum around $M = 500$. Addition of 1 wt% of P(EO-*b*-S) to the PEO/PS system causes a decrease of γ due to the surfactant effect of the copolymer, but γ is almost independent of further addition of the copolymer. The decrement of the interfacial tension $\Delta\gamma$ increases with increasing molecular weight of P(EO-*b*-S).

Keywords: Interfacial tension; Poly(ethylene oxide); Polystyrene

1. Introduction

Interfacial tension γ between immiscible polymers plays an important role in the technology of polymer alloy and has been studied long in view of pure and applied science [1–17]. As is well known, when γ of a pair of polymers A and B is high, the compatibility of them decreases and the mechanical properties of the blend become poor [1]. To improve physical properties of polymer alloys, various efforts such as reactive compatibilization have been made [18–22]. One of the fundamental issues is to understand the surfactant effect of block copolymers A–B [14–17]. So far the interfacial tensions γ between immiscible polymers have been measured for various polymer pairs, but mostly for polymers with broad distribution of molecular weight (M) [2–8]. A few studies on the dependence of γ on M have been reported [9–13]. LeGrand and Gaines [5] reported γ between the homologous series of alkanes and low molecular weight polymers. They found that γ decreased with decreasing M in proportion to $M^{-2/3}$. However, recent theories do not predict the $M^{-2/3}$ dependence of γ [23–30]. Ermoshkin and Semenov indicated that γ is proportional to 1-$k(M_A^{-1} + M_B^{-1})$ for the limit of narrow interface where k is a constant [29]. In the case where the approximation of the narrow interface does not hold, γ cannot be expressed by an analytical function [29]. Jo et al. studied theoretically the M dependence of γ and indicated that the theoretical M dependence of γ is numerically close to the $M^{-2/3}$ dependence [30]. The effect of block copolymers on γ was also studied theoretically by several authors [31]. Noolandi and Hong [32,33] calculated γ of systems composed of immiscible polymers A, B and a symmetrical diblock copolymer AB as a function of content and M of the diblock copolymer. Their result predicts that γ decreases with increasing block copolymer content and also with increasing M of the block copolymer. The structure of interface of polymer blends containing copolymers has been studied by using various methods [34].

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* Corresponding author. Tel.: +81 6 6850 5464; fax: +81 6 6848 9265.
E-mail address: k-adachi@tcct.zaq.ne.jp (K. Adachi).

[1] Present address: Prime Polymer Co. Ltd, 1-5-2 Shinbashi, Tokyo 105-7117, Japan.

[2] Present address: Nissha Printing Co. Ltd, 3-Hanai-cho, Mibu, Kyoto 604-8551, Japan.

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Those studies mentioned above were made for pairs of hydrophobic polymers. In this paper, we aim to examine the interfacial properties between hydrophilic and hydrophobic polymers. For this purpose poly(ethylene oxide) (PEO) and polystyrene (PS) have been chosen as hydrophilic- and hydrophobic polymers, respectively. An amphiphilic block polymer P(EO-*b*-S) composed of the PEO and PS blocks are used to examine the surfactant effect. As far as we know, γ of the PEO/PS interface has not been reported in literatures. We examine the M dependence of γ and the effects of diluent and P(EO-*b*-S) on γ in this system. Dioctylphthalate (DOP) is used as diluent. The data of PEO/PS/DOP system will provide data for processing of polymer alloys containing diluents. It is noted that the PEO chains possess the hydroxyl groups at the chain ends which enhance the hydrophilic nature and also cause specific interactions due to the hydrogen bonding. Koberstein et al. studied γ for pairs of immiscible polymers having the acid and base groups at the chain ends [6,35]. In the present study, we will focus on the effects of the end group of PEO, although the effects are expected to be not strong compared with those found by Koberstein et al. PEO is one of the biomedical materials [36]. Thus, the interfacial properties of PEO and hydrophobic polymer is expected to be important in such a practical application.

It is known that a droplet suspended in an immiscible medium deforms into an ellipsoid under an electric field [37–42]. In our previous papers, it was demonstrated that electric deformation of droplets is proportional to γ^{-1} [40,41]. Usually, measurements of γ between a pair of polymers are difficult due to high viscosity. We expect that the electric deformation of droplets can be used as a new method for measurements of γ and attempt to use this technique.

2. Experimental

2.1. Material

Samples of PEO were purchased from Wako Chemical Co. Ltd (Osaka, Japan). The number average molecular weights (M_n) of PEO samples were determined by the end group analysis by measurements of ^{13}C NMR for the CH_2–OH groups. These PEO samples had narrow M distribution and the polydispersity M_w/M_n of PEO was determined by GPC. Narrow distribution polystyrenes (PS-3 and PS-5) were prepared by anionic polymerization in benzene with *s*-butyllithium as the initiator. A broad M distribution sample of PS (PS-300) was purchased from Wako Chemical Co. Ltd (Osaka, Japan). The characteristics of PEO and PS are listed in Table 1. Poly(ethylene oxide-*b*-styrene) diblock copolymers P(EO-*b*-S) with narrow distribution of M were purchased from Polymer Source, Inc. (Dorval, Canada) who characterized P(EO-*b*-S) as listed in Table 2. Dioctylphthalate (DOP) (99% pure) was used without further purification.

Table 1
Molecular characteristics of PEO and PS

Code	$10^{-3}\ M_w$	$10^{-3}\ M_n$	M_w/M_n
PEO-0.3	0.29	0.26	1.1
PEO-0.5	0.53	0.48	1.1
PEO-1	0.86	0.78	1.1
PEO-2	2.1	1.9	1.1
PEO-3	2.6	2.4	1.1
PEO-8	7.5	6.8	1.1
PEO-10	9.6	8.7	1.1
PEO-30	31	28	1.1
PS-300	300	150	2.0
PS-3	3.2	2.9	1.2
PS-5	5.1	4.8	1.1

As described in Section 2.2, it is needed to increase the electric conductivity of the PEO phase in order to simplify the calculation of γ from the equilibrium electric deformation of droplets. We added 2 wt% of lithiumperchlorate ($LiClO_4$) to the PEO phase. The reason for choosing $LiClO_4$ is that the solubility of $LiClO_4$ in PEO is high and the ionic conductivity in the $LiClO_4$/PEO system works well for the enhancement of conductivity [43]. Prescribed amounts of PEO and $LiClO_4$ were dissolved in tetrahydrofuran (THF) and then THF was removed under vacuum of 10^{-2} Pa at 373 K for 12 h. Diblock copolymers P(EO-*b*-S) were also mixed with PEO in THF solutions and then THF was evaporated completely under vacuum.

Here one may wonder about the effect of $LiClO_4$ on the interfacial tension. The effect of electrolytes on γ was theoretically studied by Onsager and Samara [44]. The theory predicts that the dependence of γ on the concentration of salts is weak. In fact the data of γ of aqueous solutions of various salts indicate a weak dependence of γ on the salt concentration [45]. Thus, the effect of 2 wt% $LiClO_4$ on γ is small.

2.2. Methods

The dielectric constant and the resistivity were measured with an automatic RLC bridge (QuadTech 1693, Maynard). The experimental setup for observation of deformation of droplets was similar to that reported previously [40]. The sample holder was set in a temperature regulator made of Teflon. The separation of the electrodes was ca.1 cm. A droplet of bulk PEO was suspended in PS or PS/DOP matrices with a micro syringe. The radius of the drop was 0.2–0.5 mm. An alternating current (AC) electric field (60 Hz) of less than 5 kV/cm was applied to the sample systems. The shapes of droplets were observed with an optical microscope equipped with a video system and recorded in a personal computer. For the sake of data acquisition, measurements were repeated for one drop two or three times depending on the reproducibility. The scattering of the D values was within 8%.

It is noted that the AC field of 60 Hz is equivalent to the direct current (DC) field of the same voltage since the electric

Table 2
Molecular weights of PEO and PS blocks of diblock copolymers

Code	$10^{-3}\ M_w$(PEO)	$10^{-3}\ M_w$(PS)	M_w/M_n
P(EO-*b*-S)-4	2.1	1.8	1.2
P(EO-*b*-S)-11	7.0	3.6	1.1
P(EO-*b*-S)-53	36.4	16.4	1.1

polarization of the drop occurs much faster than 60 Hz. The relaxation time τ_P needed for polarization of a drop in which the conductivity σ_2 is much higher than the conductivity σ_1 of medium is given by the Wagner theory [45]:

$$\tau_P = \varepsilon_0(2\varepsilon_1 + \varepsilon_2)/\sigma_2 \tag{1}$$

where ε_0, ε_1 and ε_2 are the absolute dielectric constant of vacuum, the relative dielectric constants of the matrix and the drop, respectively. From σ_1 ($\approx 10^{-9}$ S m^{-1}), ε_1 (≈ 2), σ_2 ($\approx 2\times 10^{-2}$ S m^{-1}) and ε_2 (≈ 5) at 400 K, τ_P is calculated to be in the order of 4×10^{-9} S which is much shorter than the period of 1/60 s. Thus, the deformation of the droplet D is independent of $LiClO_4$ concentration.

The optimum size of droplets for measurements of electric deformation is determined by the relaxation time τ and the degree of deformation D_∞. As described below, τ increases with the drop radius b. Therefore, in order to minimize the time for measurements, small b is preferred. However, D_∞ is also proportional to b as given by Eq. (3) and hence higher electric fields are required for the measurement of D_∞ of small droplets. Since the electric field was limited to be less than 5 kV/cm, the optimum size of the drops was 0.2–0.5 mm in our setup.

The droplets deformed into ellipsoids have a circular symmetry with respect to the long axis. Thus, the value of the short axis in the three-dimensional space is the same as the observation in the two-dimensional observation. The error arises mainly from the incomplete adjustment of focus. If the edge of the ellipsoid is not in focus, clear boundary cannot be observed.

The degree of deformation D of an ellipsoidal drop is defined by $D = (X - Y)/(X + Y)$ where X and Y represent the lengths of the major and minor axes of the ellipsoid. For the case where the viscoelastic relaxation times of the drop and medium phases are much shorter than the retardation time τ of the drop deformation, $D(t)$ after application of an electric field E at time t=0 is expressed as

$$D(t) = D_\infty[1 - \exp(-t/\tau)] \tag{2}$$

where D_∞ is the equilibrium deformation [40,41]. As reported previously, τ for the electric deformation was proportional to the initial radius b and the viscosities of the drop and medium phases [40,41]. The recovery process after switching off of an electric field can be expressed by an exponential decay function. It is noted that $D(t)$ of viscoelastic droplets does not conform to Eq. (2) [42]. We regulated the experimental conditions so that τ was less than 10 min. According to Torza et al. [39], D_∞ is given by

$$D_\infty = \frac{9\varepsilon_0 K_2 b E^2 \Phi}{16\gamma} \tag{3}$$

where ε_o is the absolute dielectric constant of vacuum; b, the initial radius of the drop; K_2, the dielectric constant of the medium; γ, the interfacial free energy. Φ is a complex function of the ratios K_1/K_2, η_1/η_2, R_1/R_2, and ω where the suffixes 1 and 2 refer to the drop and matrix phases, respectively, and K, η, R, and ω represent the dielectric constant, viscosity, resistivity, and angular frequency of the applied AC field, respectively [39]. When $R_2 \gg R_1$, the drop and matrix phases can be regarded as a conductor and an insulator, respectively, and hence K_1 can be regarded to be infinity. In this case Φ becomes unity. In the present system $LiClO_4$ was added to the drop phase (PEO) as mentioned in Section 2 and the conductivity of the drop phase was of the order of 10^{-6} S while that of matrix was ca. 10^{-11} S. Therefore, the present systems well satisfy the condition of $\Phi = 1$.

3. Results and discussion

3.1. Deformation of PEO droplets in bulk PS

Fig. 1 shows the representative D versus time (t) curves at 405 K for droplets of PEO-8 suspended in PS-3. Various electric fields were applied at $t = 0$. As shown in this figure the deformation increases with increasing E. After reaching an equilibrium deformation, the electric field was switched off at the time indicated by the arrow. Similar behaviour was observed for PEO droplets suspended in PS-5. Those data conformed well to the theoretical curves (Eq. (2)) and D_∞ was determined from the plateau value.

Fig. 2 shows the E^2 dependence of D_∞ of PEO droplets with various number average molecular weight (M_{PEO}) in the matrix of PS-3. Since the deformation depends on the size b of the drops and the dielectric constant K_2 of the medium as well as E, the abscissa is normalized by the factor of $9\varepsilon_0 K_2 b/16$ as shown in this figure. Here, the dielectric constant K_2 of PS at 405 K was measured to be 2.5 ± 0.1. We see that the plots conform to straight lines starting from the origin. The slopes of these lines are equal to $1/\gamma$ as indicated by Eq. (3). Fig. 3 shows the M_{PEO} dependence of γ thus determined.

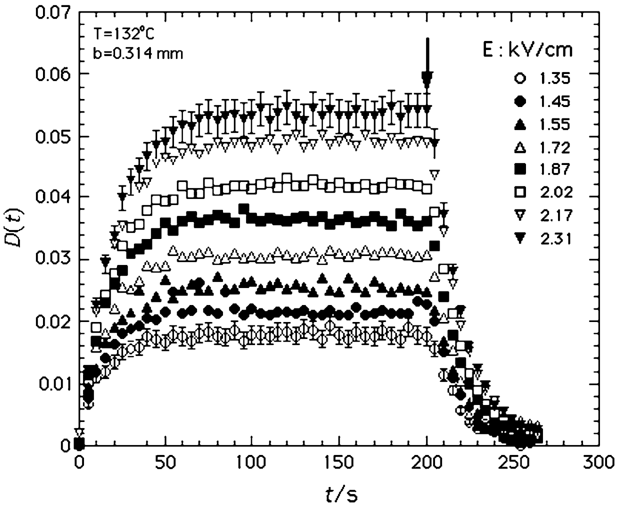

Fig. 1. Time t dependence of the degree of deformation D at 405 K for droplets of PEO-8 suspended in PS-3. The arrow indicates the time at which the applied electric field was switched off. Applied electric fields E in kV/cm and radius b in mm of the drops are given in this figure. Error bars are indicated only for the data of $E = 1.3$ and 2.31 kV/cm.

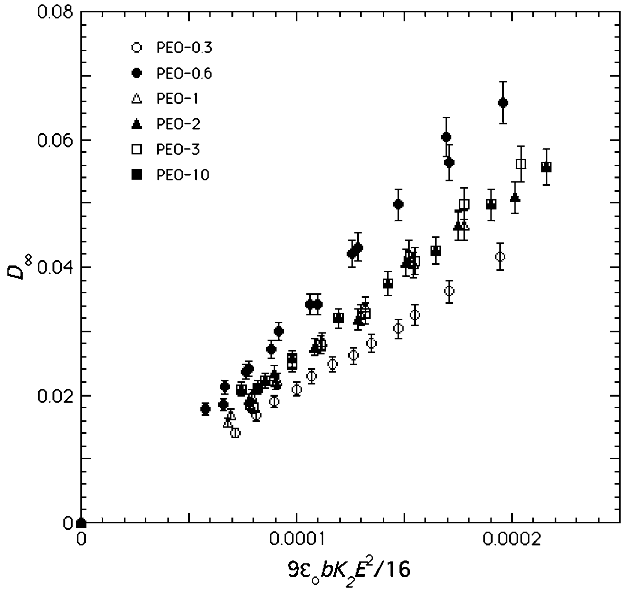

Fig. 2. Plots of D_∞ versus $9\varepsilon_0 K_2 bE^2/16$ for PEO drops with various M at 405 K.

Before discussion of the result, we consider the relationship between γ and the retardation time τ observed in Fig. 1. Previously, we found that τ can be expressed by a form [40,41]:

$$\tau = \frac{(\alpha\eta_1 + \beta\eta_2)b}{\gamma} \tag{4}$$

where α and β are the factors close to unity and η_1 and η_2 are the zero shear viscosities of the drop and medium, respectively. For the interface of poly(propylene oxide)/poly(dimethyl siloxane), Nishiwaki et al. [41] reported that $\alpha = \beta = 1.0 \pm 0.2$. In the present system, the viscosity of PS is much higher than PEO and hence $\eta_1 << \eta_2$. Thus, if $\beta = 1$ is assumed, γ can be determined from τ as well as D_∞. This method is similar to the drop retraction method [7,15]. However, since the viscosity is sensitive to temperature, the error becomes relatively large if the temperature regulation is not very accurate. Therefore, we did not use the data of τ for the determination of γ.

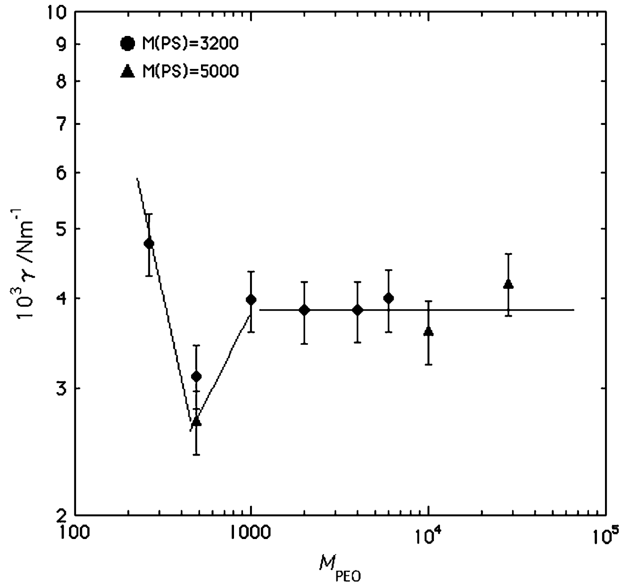

Fig. 3. Dependence of γ on the number average molecular weight M_{PEO} of PEO for the interface of PEO and PS-3 or PS-5.

Returning to Fig. 3 we see that γ at the lowest M_{PEO} (=260) is the highest. With increasing M_{PEO}, γ reaches minimum at about $M_{\mathrm{PEO}} = 480$ and in the range of $M_{\mathrm{PEO}} > 1000$, γ becomes almost independent of M_{PEO}. This complicated behaviour may be explained by considering two competitive effects: the monomer–monomer interactions and the effect of the end groups. The monomer–monomer interactions are the major origin of γ. Helfand and coworkers [23–25] proposed the theories of γ_∞ of polymers A and B with infinitely high M:

$$\gamma_\infty = T\left[\frac{\beta_A + \beta_B}{2} + \left(\frac{1}{6}\right)\frac{(\beta_A - \beta_B)^2}{\beta_A + \beta_B}\right]\left(\frac{\chi}{6}\right)^{1/2} \tag{5}$$

where T is temperature, χ the interaction parameter between A and B, and $\beta_i = a_i/v_i$ with a the segment length and v the segment volume. Ermoshkin and Semenov calculated γ for the case of finite M [29]. For the case of the narrow interface γ is given by

$$\gamma = \gamma_\infty\left[1 - K\left(\frac{1}{\chi N_A} + \frac{1}{\chi N_B}\right)\right] \tag{6}$$

where $K = 2\ln 2$ and N_A and N_B are the number of statistical segments. The narrow interface corresponds to $\chi N_i \gg 1$. For the case of $\chi N_i \approx 1$, γ cannot be expressed by an analytical function. The Ermoshkin–Semenov theory [29] and other theories [26–28,30] commonly predict that in the high M region, γ is almost independent of M, but γ decreases with decreasing M in the low M region. We see in Fig. 3 that γ is almost independent of M_{PEO} in the high M range, but decreases with M_{PEO} around $M_{\mathrm{PEO}} \approx 500$–$1000$. This behaviour is attributed to the monomer–monomer interactions.

The high value of γ at $M_{\mathrm{PEO}} = 260$ can be attributed to the effect of the hydroxyl groups (OH) at the chain ends. It is known that the relationship between γ and the surface free energies σ of the components 1 and 2 is approximately given by [3]:

$$\gamma = \left(\sqrt{\sigma_1^d} - \sqrt{\sigma_2^d}\right)^2 + \left(\sqrt{\sigma_1^p} - \sqrt{\sigma_2^p}\right)^2 \tag{7}$$

where the superscripts d and p refer to the dispersion and polar force components of the surface free energies, respectively, and the subscripts 1 and 2 denote the component polymers. With decreasing molecular weight of PEO, the contribution of the OH group to the polar component of σ_2^p increases and hence γ increases rapidly in the low M region. Thus, we can explain the results shown in Fig. 3. For further discussion of the M dependence of γ in the low M region, we need more data in this M_{PEO} region.

3.2. Molecular weight dependence of γ

In addition to the bulk PEO/PS system, we also measured γ of the interface formed between bulk PEO and 40 wt% PS-300 solution in dioctylphthalate (PS/DOP(40)). In this section we examine the M dependences of γ for the PEO/PS and PEO/(PS/DOP(40)) systems. Before measurements of γ on the PEO/(PS/DOP(40)) system, it was confirmed that PEO drops suspended in PS/DOP(40) matrix did not swell appreciably. This indicates that PEO is not miscible in DOP or PS/DOP solutions. The miscibility data between PEO and DOP are not available in literature. From the resolution of our setup, the miscibility of DOP in PE is estimated to be less than 0.5 wt%.

The behaviour of electric deformation of PEO drops in this medium was similar to PEO/bulk PS blends, but D_∞ was larger than that of bulk PS if compared at the same E indicating that γ in the PEO/(PS-300/DOP(40)) system is smaller than the bulk system as listed in Table 3. It is seen that γ in the PEO/(PS-300/DOP(40)) system decreases with decreasing M_{PEO}.

In the measurements of γ on the bulk system, we used low M PEO and PS. In the solution system, DOP acts to broaden the interface. Therefore, for both of the bulk and solution systems, we expect that the approximation of the narrow interface is poor and Eq. (6) is not applicable. Although the Ermoshkin–Semenov theory provides the theoretical equations for the calculation of γ in the case of the broad interface, the numerical calculation of γ is rather difficult [29]. Jo et al. [30] calculated theoretically the M dependence of γ based on the broad interface model proposed by Vrij [46]. They found that the M dependence of γ can be numerically close to the M dependence proposed empirically by LeGrand and Gaines [5]:

$$\gamma = \gamma_\infty - CM^{-2/3} \tag{8}$$

where C is the constant. Thus, we compared the M dependences of γ with Eq. (8). Fig. 4 shows the dependence of γ of the PEO/PS and PEO/(PS-300/DOP(40)) systems on $1/M_{\mathrm{PEO}}^{2/3}$. Since the effect of the end groups becomes dominant in the low M region, the plots are made in the range of $M_{\mathrm{PEO}} > 480$. It is seen that γ is not linear with respect to $M_{\mathrm{PEO}}^{-2/3}$ in this M region for the both systems.

3.3. Influence of diluent on γ

Vrij proposed a theory of the interfacial tension of immiscible polymers 1 and 2 which contain a common solvent [46]. Vrij calculated the interfacial free energy γ assuming a broad interfacial region of the order of chain dimension:

$$\gamma = \left(<s^2>/6\right)^{1/2} \Omega \sigma_r \phi_{\mathrm{p}}^2 \tag{9}$$

where $<s^2>$ is the mean square radius of gyration, Ω the parameter depending on the interaction energies, σ_r the function of temperature, and ϕ_{p} the volume fraction of the polymers. Thus, the theory predicts that γ at $\phi_{\mathrm{p}} = 0.4$ is smaller than γ of the bulk system by a factor of 0.16. In the present system, the profile of the composition at the interface is not symmetrical. In spite of this difference the theory explains approximately the ratio of γ between the bulk and solution systems, i.e., γ of the PEO/(PS-300/DOP) system is 0.25–0.2 of γ of the bulk PEO/PS system.

Table 3
Interfacial tension γ between PEO and PS-300/DOP(40) at 373 K

Drop phase	Medium	γ/mN m^{-1}
PEO-1	PS-300/DOP(40)	0.61
PEO-2	PS-300/DOP(40)	0.85
PEO-6	PS-300/DOP(40)	1.2
PEO-20	PS-300/DOP(40)	1.5

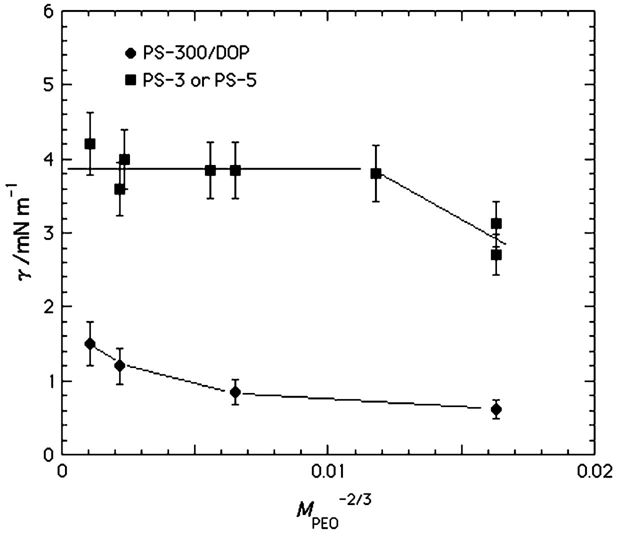

Fig. 4. Dependence of γ on $M_{\mathrm{PEO}}^{-2/3}$ for PEO/PS and PEO/(PS/DOP(40)) interfaces.

It is known that the thickness of the interface of bulk polymers is narrower than that assumed by Vrij [46]. According to Helfand and Sapse (HS), γ is proportional to $\chi^{1/2}$. For a ternary system of polymer/polymer/common solvent, the effective interaction parameter χ' decreases to $\chi\phi_{\mathrm{p}}$. Thus, the HS theory predicts that γ is proportional to $\phi_{\mathrm{p}}^{1/2}$ and hence the predicted ratio of γ between the 40% solution and bulk systems is 0.63. This theoretical ratio is higher than the present observation. We speculate that although DOP molecules do not penetrate into the bulk drop phase, they penetrate into the interfacial region and the PEO/(PS-300/DOP) system forms relatively broad interfacial region resulting in the decrease of γ.

3.4. Effect of P(EO-*b*-S) diblock copolymer on γ

The effect of diblock copolymer on γ of the bulk PEO-8/PS-3 system was examined by mixing small amounts of P(EO-*b*-S)-4, P(EO-*b*-S)-11, and P(EO-*b*-S)-53 in PEO-8. Since the mixture of PEO-8 and P(EO-*b*-S)-53 exhibited macroscopic phase separation, the concentration of the copolymer was limited in the range less than 1 wt%. The behaviour of electric deformation curves in these systems was similar to the system without the copolymers. Thus, γ was determined in the same manner as described above. The results are listed in Table 4.

It is seen that by addition of 1 wt% of the diblock copolymers to the PEO-75, γ decreases from 3.8 to 1.5 ± 0.5 mN/m and the further increase of the copolymers does not cause large changes of γ. This indicates that the adsorption of the copolymers at the interface is saturated by addition of the copolymer less than 1 wt%. It is seen in Table 4 that γ decreases with increasing M of the copolymer. Although the ratio of the PS and PEO block molecular weights of these copolymers are not fixed, γ is plotted with respect to the total molecular weight M_b of the copolymer in Fig. 5. We see that γ is approximately linear to log M_b.

Noolandi and Hong calculated γ for a system composed of two homopolymers A, B, block copolymer AB, and solvent S based on a mean field theory [32,33]. They calculated γ for a symmetric system: $N \equiv N_A = N_B = \infty$, $N_b \equiv N_{bA} = N_{bB}$ where N is the degree of polymerization, and suffices bA and bB represent the block chains A and B of the block copolymer. The interaction parameters χ_{AS} and χ_{BS} between S and the polymers A or B are assumed to be zero. The change of the interfacial tension $\Delta\gamma$ by addition of the block copolymer AB to the bulk A/B system is given by

$$\Delta\gamma \cong \varphi_b d\left(\frac{\chi}{2}+\frac{1-\exp(N_b\chi/2)}{N_b}\right) \le -\frac{\varphi_b d\chi^2 N_b}{8} \qquad (10)$$

where d is a constant representing the width of the interphase, φ_b the volume fraction of the block copolymer, and χ the interaction parameter. One of the differences between the present system and the model used in the theory is that the theory assumes that the molecular weights of A and B are infinitely high while in our experiment, the molecular weight of PEO and PS is similar to the block copolymer. However, this difference may not affect much the M_b dependence of γ since Noolandi and Hong [32] performed numerical calculation of γ between A and B containing AB and indicated that the effect of M of A and B on γ was not strong (see Figs. 4 and 5 of Ref. [32]).

The theory (Eq. (10)) predicts that γ decreases with increasing molecular weight M_b and φ_b of the block copolymer. However, the present results indicate that γ is almost independent of φ_b in the range of the copolymer content used in this study. This indicates that the critical micelle concentration φ(cmc) of P(EO-*b*-S) in PEO is lower than 1 wt% and only a part of P(EO-*b*-S) is dissolved in the PEO phase. Thus, the effective concentration of P(EO-*b*-S) remains constant. Leibler et al. [37] indicated theoretically that φ(cmc) decreases rapidly with increasing M_b. Therefore, the M_b dependence of γ shown in Fig. 5 is due to two competitive effects: the decrease of the effective copolymer concentration and the increase of the surfactant effect of the block copolymer with increasing M_b. Although the free energy ΔF for formation of micelles has been calculated theoretically by Libler et al. [47] and Noolandi and Hong [32], ΔF is composed of several terms and φ(cmc) cannot be given by a simple analytical function of M_b. Therefore, detailed comparison with the theory and experimental result is difficult. The result shown in Fig. 5 indicates that the M_b dependence of the surfactant effect is slightly stronger than the M_b dependence of φ(cmc).

Table 4
Interfacial tension γ (mN/m) between PEO-8 containing P(EO-*b*-S) and PS-3

System	Content (wt%) of P(EO-*b*-S) in PEO-8					
	0.5	1	2	3	4	6
[PEO-8/P(EO-*b*-S)-4]/PS-3	–	–	2.1	1.8	2.0	2.0
[PEO-8/P(EO-*b*-S)-11]/PS-3	–	1.5	1.5	1.4	1.4	–
[PEO-8/P(EO-*b*-S)-53]/PS-3	1.0	1.0	–	–	–	–

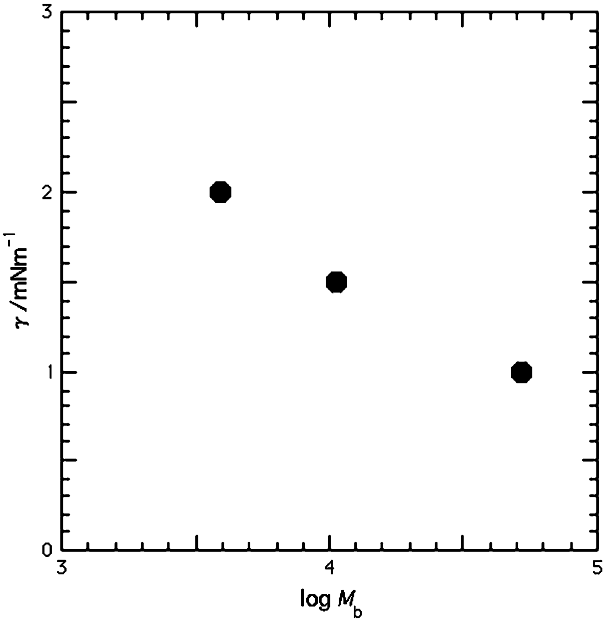

Fig. 5. The plateau value of γ versus molecular weights of P(EO-*b*-S).

4. Conclusion

The interfacial tension γ between poly(ethylene oxide) PEO and polystyrene PS was measured by utilizing electric deformation of droplets and the effects of diluent and poly(ethylene oxide-*b*-styrene) diblock copolymer P(EO-*b*-S) on γ were examined. It was found that this method is relatively handy and is suited for measurements of γ between highly viscous polymers. The dependence of γ on molecular weight of PEO (M_{PEO}) has been examined: γ at the lowest M_{PEO} (=260) is highest and with increasing M_{PEO}, γ reaches a minimum at about $M_{PEO} = 480$ and in the range of $M_{PEO} > 1000$, γ becomes almost independent of M_{PEO}. This complicated behaviour can be explained by considering the polar contribution of the interfacial energy of the end OH groups. The interfacial tension between bulk PEO and 40% DOP solution of PS is smaller than the bulk system and increases slightly with increasing M_{PEO}. The result can be explained approximately with Vrij theory indicating that the diluent acts to increase the interfacial region. In both of the bulk PEO/PS and PEO/PS solution systems, γ does not conform to the $M^{-2/3}$

dependence. When 1 to 6 wt% of P(EO-*b*-S) is added to PEO, γ decreases due to the surfactant effect of the diblock copolymer. With increasing molecular weight M_b of the diblock copolymer γ decreases slightly, but is almost independent of the content φ_b of the block copolymer. This indicates that the critical micelle concentration φ(cmc) of P(EO-*b*-S) in PEO is lower than 1 wt%. The result can be explained by considering the competitive two effects, namely the decrease of the effective concentration and the increase of the surfactant effect of the block copolymer with increasing M_b. The M_b dependence of the surfactant effect is stronger than the M_b dependence of φ(cmc).

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