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Polymer 46 (2005) 2811–2816

polymer

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Studies on some factors influencing the interfacial tension measurement of polymers

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Received 24 September 2004; received in revised form 6 January 2005; accepted 7 January 2005

Abstract

To improve the accuracy of polymer interfacial tension measurement using deformed drop retraction method (DDRM), we examined some factors, such as the shape parameter, the retraction scale D_0, and the distortion criterion γ by means of dissipative particle dynamics (DPD) simulation with 6 different models and analysis with three observation data, and proposing a new shape parameter P. Results show that the shape parameter order of suitable to various retraction scales and larger distortion is $P > (a^2 - b^2) > D$. This study found that choosing a suitable retraction scale is very important, and that $D_0 \cong 0.15$ is the most suitable retraction scale in DDRM measurement. In the scale, the three shape parameters cannot make much difference on the measurement deviation from the standard. This study also found that the distortion criterion γ varies with different shape parameters. We also found here when $D_0 \cong 0.15$ the distortion criterion becomes $\gamma < 0.15$, and one has a reliable measurement with any shape parameter.

Keywords: Dissipative particle dynamics; Deformed drop retraction method; Shape parameter

1. Introduction

Interfacial tension plays a predominant role in multiphase systems, such as polymer blends and alloys. Many attempts have been made to develop accurate and convenient techniques to measure the interfacial tension of the blend [1–4]. The different techniques can generally be divided into three catalogues: equilibrium methods, dynamic methods and rheological methods.

The dynamic methods are used more broadly than the other two. The main reason is that dynamic methods are more convenient and take a shorter time. The methods take advantage of the balance between the interfacial forces and other factors such as thermal disturbances [2–5]. It is based on shape evolution of fluid drop from a non-equilibrium state to an equilibrated state. Three main approaches: breaking thread method (BTM) [6–9], imbedded fiber retraction method (IFRM) [1,10–11] and deformed drop retraction method (DDRM) [2,3,5,12] are included in this catalogue.

DDRM overcame limitations of BTM and was a derivative of IFRM [2]. Luciani proposed it firstly in 1997 [2]. The principle of DDRM is to measure dimensions of an ellipsoidal drop in its evolution to a sphere shape. Luciani presented the following theoretical equation to describe the shape evolution:

$$D = D_0 \exp\left\{ -\frac{40(p+1)}{(2p+3)(19p+16)} \frac{\sigma}{\eta_m R_0} t \right\} \quad (1)$$

where D is the drop shape parameter defined by Taylor [13] as $D = (a-b)/(a+b)$, a is the major axis of ellipsoid and b is the minor as showed in Fig. 1. D_0 is initial value of D at $t=0$. p is viscosity ratio of dispersed to matrix phase and σ is their interfacial tension. η_m, R_0 and t is viscosity of matrix, final radius of sphere drop and time of retraction, respectively. In the process of ellipsoidal drop retraction, p, η_m and R_0 are constant. σ is calculated from slope of $\ln(D/D_0)$ versus time t.

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doi:10.1016/j.polymer.2005.01.073

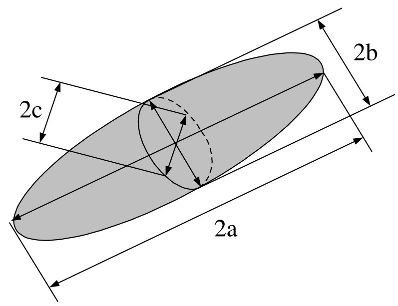

Fig. 1. Schematic representation of an ellipsoidal drop.

Recently, experimental details of DDRM were markedly developed. In the experiment of Luciani, only one dimension of the ellipsoid can be measured, which is the short axis [2]. They have to assume the two short axes are equal and then according to the constant volume to calculate the length of long axis. Zhou proposed a new method to measure simultaneously two dimensions, which are axes a and b [3]. This progress made accuracy of the measurement enhanced.

However, there are still some problems in the measurement of interfacial tension for DDRM. In calculating the interfacial tension, use of Eq. (1) basically asks that D is limited to a small deformation, which was defined by Taylor as a convenient parameter for expressing deformed drops [13]. Luciani, who used D to calculate interfacial tension, also noticed this point and assumed the low levels of ellipsoid deformation in DDRM determination of the interfacial tension [2]. However, experimentally it is not simple to master this scale to be small enough. Since D expresses the drop shape, zero will be the D when the shape reaches the equilibrium, a sphere. Choosing a very small D as the initial state in the experiment may lead to a bad linearity of the data against a reliable slope. Actually, in experiments, people adopted different initial states, such as $D=0.16$ in Luciani measurement [2], and $D=0.15$ and 0.38 for Xing [5] and Zhou [3]. The deformation degrees in their experiments were different. On the other hand, D may not be the best parameter for evaluating a dynamic process due to its insensitivity to drop dimensions [14]. Zhou using his new technique found that in most cases the volume of the ellipsoid in the retraction is not constant, or the two short axes are not in the same length [3]. In order to represent the real deformation of a drop when three axes of the ellipsoid appear different, Zhou then proposed a new parameter (a^2-b^2) to replace D. In our previous study [15], we investigated Zhou's parameter and found it is better than D in a retraction process. Since it concerns a larger scale change in deformed shape of the ellipsoid, it is unclear about the orientation of the parameters if the process is just small deformation [2,5]. Additionally, the parameter, (a^2-b^2), only includes information of two dimensions, a and b, and it thus provides a chance to include the third dimension, c, for promoting the parameter. To obtain better understanding of the above problem and possibility, it obviously needs a further study.

In the present work, we used dissipative particle dynamics (DPD) simulation method to examine how various shape parameters work in the retraction processes, especially in the case that three of the axes of the ellipsoid are different in the initial state. The present study extracted three DDRM experiment data, and used the available shape parameters to calculate the interfacial tensions, and also selected different regions to fit the equation. Additionally, we proposed a new parameter P. Results show that P is even better than D and (a^2-b^2) in decreasing the influence of the axial difference at the initial state, and obtain a reasonable measurement.

2. Method and models

DPD is a mesoscale simulation method, wherein the system is represented by a set of discrete particles of equal mass placed in a three-dimensional (3D) simulation box [16–19]. The DPD particles interact pairwise, and are subject to repulsive conservative forces, dissipative forces, and random forces associated with interactions with surrounding particles within a specified cutoff radius. Recent studies showed that DPD is feasible in simulation of a system with interfacial tension [1,20–23]. In our simulation, the box, which was subjected to the usual periodic boundary conditions, contains 48000 particles in $20\times20\times20$ cubes. There are two kinds of particles in the box, which form a drop and a matrix, respectively. The parameters of the conservative forces, between the same kinds of particles are 12.5 and between different are 18. There is no difference between particles of any kinds in their dissipative interaction, which was decided by random parameter. Groot established through trial and error that the optimum value of random parameter meeting the requirements of fast temperature equilibration, rapid convergence and stability is 3, and time step is 0.04 [17]. To get more stable system and more accurate results while get dynamic properties not very slowly, we choose time step as 0.02 and temperature as 0.12.

Calculating method of interfacial tension is simplified in the present study. Irving–Kirkwood method is popular in simulation of measuring interfacial tension between two materials [24]. It is suitable for a static system. However, DDRM describes a kinetic process, and extracts the interfacial tension from evolution of the drop shape. Our measurement of the interfacial tension is different from the method, but follows the experiment. DDRM process finds the polymer drop evolution from an ellipsoid to a sphere. Taylor [13] and Luciani [2] found the relationship:

$$\ln P = Kt \tag{2}$$

where P is a shape parameter, which is a function of the axes of the ellipsoid, and t is time. K is slop and is a constant for a two-polymer-blend system, and $K = \sigma C$, σ is the interfacial tension, C is constant. In the present study, we obtained $\sigma = K \cdot \sigma_0 / K_0$, where σ_0 and K_0 are the standard tension and the standard slop.

Determination of ellipsoid geometry is a little difficulty in DPD simulation since the calculating box consists of thousands dynamic particles. The thermal fluctuation in a DPD simulation heavily affects the observation of the ellipsoid shape. In the present study, the author through trial and error presented a cellblock scanning method to measure the drop size. Firstly, find central point of the ellipsoid and set the point as an origin of a coordinate. Then the inertial tension of the drop-particles was calculated. Meantime, the eigenvectors were used as coordinate translation matrix, using which three ellipsoid axes a, b, and c were overlapped with the system axes X, Y and Z. A cellblock, which consists of 27 cells, was used to scan the simulation box along system axes. 6 acmes of the ellipsoid will be found. Then using nonlinear least square method to fit ellipsoid equation with the coordinates of 6 acmes. Lastly, a more accurate geometry will be got. Details can be found in our previous article [15]. The geometry data of the ellipsoid were used to fit a kinetic equation that involves the interfacial tension.

Using DPD simulation method, 6 kinds of ellipsoid models were examined to study the retraction scale influence on measurement of interfacial tension using various shape parameters, as showed in Table 1. In the simulation system, all the conditions except geometries of the six models are the same, which means the calculated interfacial tensions should be the same. The six models have the same long axis and the same volume, which amounts to 452. The difference is the length of two short axes. Model 1 is an equal-short-axis ellipsoidal drop and the others are unequal-short-axis drops.

3. Results and discussion

3.1. Comparison with three experimental data

In order to expose the characters of the two shape parameters, D and $(a^2 - b^2)$, we made further comparison with three experimental data. These observed experimental data were extracted from the retraction processes, such as showed in Luciani's Fig. 4 [2], Xing's Fig. 11 [5] and Zhou's Fig. 5 [3]. Then calculated interfacial tension as showed in Table 2. σ_1 is calculated using D while σ_2 is using $(a^2 - b^2)$. First, we reproduced the original interfacial tensions according to the same method. The values we calculated for Luciani, Xing and Zhou are 1.32×10^{-3}, 6.79×10^{-3} and 0.642×10^{-3} N/m, respectively. Comparing with the original data 1.5×10^{-3}, $6.8 \pm 1.8 \times 10^{-3}$ and 0.62×10^{-3} N/m, we found that the last two data, $\sigma_1 = 6.79$ and $\sigma_2 = 0.64$ are well reproduced, but the first value $\sigma_1 = 1.32$ is somehow deviated from the original value. However, Zhou [3] found the similar problem when he extracted the same data from Luciani's Fig. 4, and using $(a^2 - b^2)$ to calculate the interfacial tension and obtained $\sigma_2 = 1.42$, which is also obvious departure from Luciani's data 1.5. However, the value of 1.42 is close to our calculation $\sigma_2 = 1.40$. The close data from both Zhou's resources and ours indicate that the reproduction in the present study is possibly reliable. Secondly, we compared values of σ_1 and σ_2 to the literature data and found that σ_2 is larger than corresponding σ_1 in all the cases, and that both values appear with relatively small difference, and that it seems using $(a^2 - b^2)$ results in a better interfacial tension measurement than using D.

3.2. Three scales in retraction process

Degree of the small deformation of ellipsoid has not been clearly quantified so far. To find suitable scale of the retraction, we defined three scales: scale 1 (whole range of data), scale 2 ($\sim$last 2/3 data) and scale 3 ($\sim$last 1/2 data) as showed in Fig. 2. The three scale processes have different D_0 at the beginning of their retractions. The values of D_0 and σ are calculated, respectively, as showed in Table 3. Both the values of σ_1 and σ_2 show that when D_0 in the scale of 0.15–0.17, the values are close to literature data. In the other scope of D_0 almost all the σ values deviate to certain extent from literature data.

3.3. A new shape parameter

Since a and b are only two axes of ellipsoid as showed in Fig. 1, D and $(a^2 - b^2)$ are limited to express the full shape information of ellipsoid with three different axes. To improve the accuracy of $(a^2 - b^2)$, in the present study, we replace b by m, which $m = (b + c)/2$ (c is another short axis of ellipsoid), and defined the new shape parameter as

Table 1
Dimensions of 6 kinds of ellipsoid models

Model	a	b	c	Volume
1	9	3.464	3.464	452
2	9	4	3	452
3	9	4.5	2.667	452
4	9	5	2.4	452
5	9	5.5	2.182	452
6	9	6	2	452

Table 2
Compare of interfacial tension got from three experimental data

Reference	D_0	$\sigma_1 \times 10^3$, N/m (using D)	$\sigma_2 \times 10^3$, N/m (using a^2-b^2)	Literature data ($\times 10^3$ N/m)
Luciani	0.16	1.32	1.40	1.5 (DDRM [2])
				1.6 (Thermodynamic method [25])
Xing	0.15	6.79	7.07	6.8±1.8 (DDRM [5])
				8.4±1.5 (BTM [5])
				7.5±1.4 (IFRM [5])
				7.2±0.1 (PDM [5])
				7.2±2.0 (Palierne Model [5])
				7.1±2.0 (Bousmina Model [5])
Zhou	0.38	0.565	0.642	0.62 (DDRM [26])
				0.68 (Spinning drop method [27])
				1.25 (Shear oscillation method [28])
				0.6 (Rheological method [29])
				1.11 (Nwumann triangle method [30])

σ_1 is calculated using D and σ_2 using (a^2-b^2).

$P=a^2-m^2$. P includes all the three dimensional message of an ellipsoidal drop.

3.3.1. Confirmation from experimental data

We compare the shape parameters D, (a^2-b^2) and P with one set of experimental data of Fig. 5 of Zhou [3] as showed in Figs. 3–5. σ_1, σ_2 and σ_3 are calculated, respectively, from slope of $\ln(D/D_0)$, $\ln((a^2-b^2)/(a^2-b^2)_0)$ and $\ln(P/P_0)$ versus time t. In turn their values are 0.565×10^{-3}, 0.642×10^{-3} and 0.614×10^{-3} N/m separately. The last one is more close to that of Yu, 0.62×10^{-3} N/m [26].

We examined the shape parameter P at three scales of the retraction of Zhou [3] as showed in Table 3. Both the values of σ_3 at the three scales are close to literature data. So we conclude that P is better in measuring interfacial tension.

3.3.2. Confirmation from simulation data

Different initial geometries of the ellipsoid are mostly encountered in experiments. We designed six models and examined systematically the influence of different geometries on the interfacial tension measurement, using different shape parameters. In Table 4, Model 1 is taken as a standard since it is an equal-short-axis ellipsoid, which is an ideal shape of DDRM. K_3 and σ_3 is the slope and the tension corresponding to the new parameter P. 'Dev' means the relative deviation of each σ from the reference value. Model 2 is used here as a reference for $\sigma=0.62$ since it uses the same initial geometry as in experiment [3]. The Model 2 produces a slope, which is the reference slope. Then both the reference σ and the reference slope were used to calculate the other σ. Among the data in Table 4, the relative deviations of σ_3 are all below 10%, while those of σ_1 all high than 10% and half of σ_2 are lower than 10%. Using the new shape parameter P, the distortion of ellipsoid geometry has little influence on measurement of interfacial tension.

3.4. The distortion criterion γ

As showed in Table 1 from Model 1 to Model 6, departure from the initial geometry of ellipsoid, $b=c$, is getting more serious Since D_0 is only two-dimensional parameters it is hard to describe the degree of the initial geometry distortion. D_0 here in Table 4 shows an opposite behavior against the distortion enhancement. To reflect

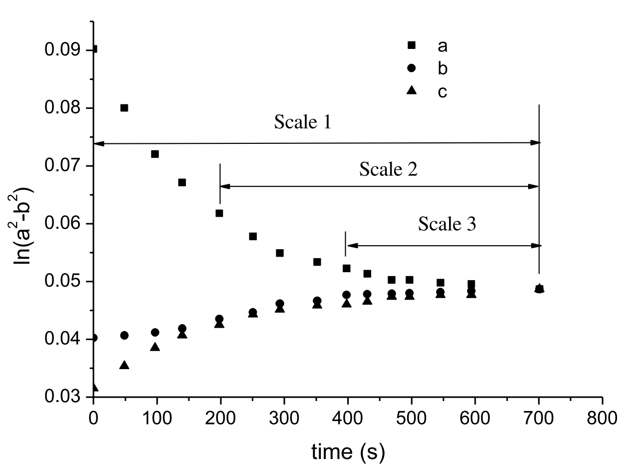

Fig. 2. Scale representation of Zhou experimental data.

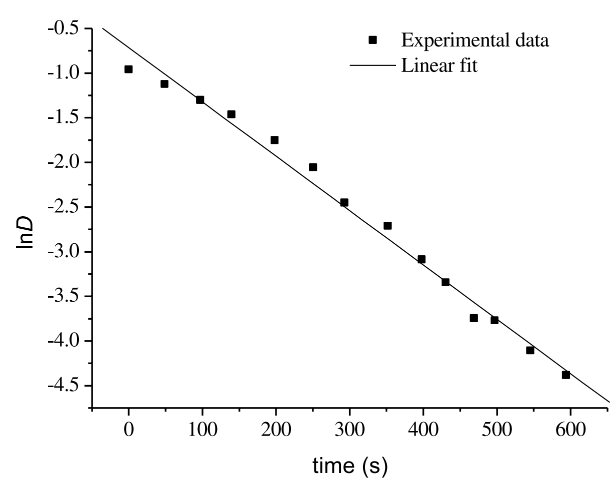

Fig. 3. Time evolution of shape parameter D for data of Zhou.

Table 3
Compare of interfacial tension got from three stages of one retraction process

Items	Luciani			Xing			Zhou		
	Scale 1	Scale 2	Scale 3	Scale 1	Scale 2	Scale 3	Scale 1	Scale 2	Scale 3
D_0	0.16	0.09	0.04	0.15	0.10	0.05	0.38	0.17	0.05
Observation $\sigma \times 10^3$, N/m	1.5			6.8			0.62		
$\sigma_1 \times 10^3$, N/m	1.32	1.26	1.02	6.79	7.65	7.89	0.565	0.633	0.601
$\sigma_2 \times 10^3$, N/m	1.40	1.31	1.04	7.07	7.84	7.99	0.642	0.664	0.619
$\sigma_3 \times 10^3$, N/m							0.614	0.619	0.593

σ_1 is calculated using D, σ_2 using (a^2-b^2) and σ_3 using P, which will be discussed in Section 3.3.

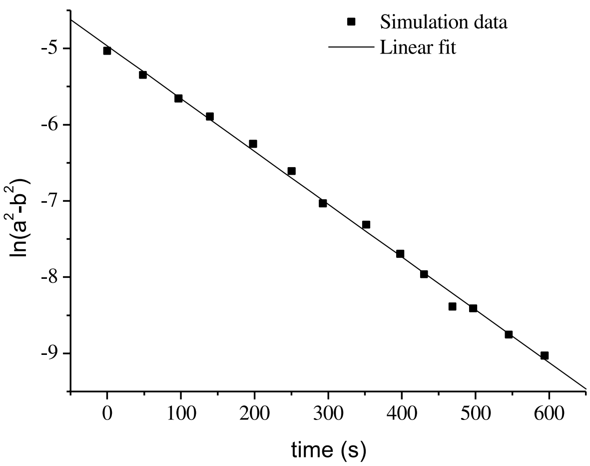

Fig. 4. Time evolution of shape parameter (a^2-b^2) for data of Zhou.

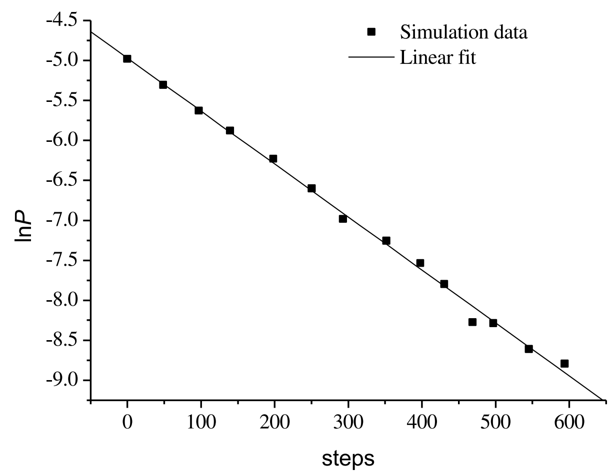

Fig. 5. Time evolution of shape parameter P for data of Zhou.

effectively a shape message, in our previous study, we defined a factor $\gamma=(b-c)/a$ to describe the initial geometry of ellipsoid [15]. In Table 4, the value of γ increases with the distortion of the initial geometry. If $\gamma>0.3$, the value of σ_2 by using (a^2-b^2) will be beyond the error 10%, which is consistent with our previous study [15]. In the present study, we found using different shape parameter the distortion criterion γ varies. When Using D the γ must be smaller than 0.2 as the criterion, while using P the γ can be as larger as 0.4 to keep all the model errors under 10%. This result is concerned with a larger scale retraction $D_0>0.2$.

In Section 3.2, we find the most applicable scale of D_0 is 0.15–0.17. So we shifted our simulation data on a new starting point $D_0 \cong 0.15$ and calculated all the data listed in Table 5. The data show that if $D_0 \cong 0.15$, the criterion value γ should be adjusted to 0.15. That is when $\gamma<0.15$ the relative deviation ofσ_1, σ_2 andσ_3 are almost all bellow 10%.

4. Conclusion

In the present study, in order to have a better understanding of some factors influencing the interfacial tensions measurement, such as the shape parameter, the retraction scale, and the distortion criterion, we made DPD simulation with 6 different models and analysis with three observation data, and proposed a new shape parameter P. The results

Table 4
Interfacial tension and relative deviation of 6 models ($D_0>0.2$)

Model	D_0	γ	K_1 ($\times 10^4$)	σ_1 ($\times 10^3$, N/m)	Dev (%)	K_2 ($\times 10^4$)	σ_2 ($\times 10^3$, N/m)	Dev (%)	K_3 ($\times 10^4$)	σ_3 ($\times 10^3$, N/m)	Dev (%)
1	0.43	0.0	−2.027	0. 73	0	−2.810	0. 60	0	−2.612	0. 65	0
2	0.39	0.2	−1.733	0. 62[a]	15.1	−2.883	0. 62[a]	3.3	−2.497	0. 62[a]	4.6
3	0.34	0.2	−1.615	0.58	20.5	−2.564	0.55	8.3	−2.424	0.60	7.7
4	0.29	0.3	−1.359	0.49	32.9	−2.417	0.52	13.3	−2.367	0.59	9.2
5	0.25	0.3	−1.079	0.39	46.6	−2.326	0.50	16.7	−2.405	0.60	7.7
6	0.21	0.4	−1.000	0.36	50.7	−2.291	0.49	18.3	−2.441	0.61	6.2

[a] The reference σ is from Model 2 in Zhou's experiment [3], γ will be discussed in Section 3.4.

Table 5
Interfacial tension and relative deviation of 6 models ($D_0 \cong 0.15$)

Model	γ	K_1 ($\times 10^4$)	σ_1 ($\times 10^3$, N/m)	Dev (%)	K_2 ($\times 10^4$)	σ_2 ($\times 10^3$, N/m)	Dev (%)	K_3 ($\times 10^4$)	σ_3 ($\times 10^3$, N/m)	Dev (%)
1	0.07	−2.983	0. 66	0	−3.239	0.65	0	−2.722	0.67	0
2	0.10	−2.812	0.62[a]	6.1	−3.088	0.62[a]	4.6	−2.501	0.62[a]	7.5
3	0.12	−2.670	0.59	10.6	−2.967	0.60	7.7	−2.559	0.63	6.0
4	0.13	−2.869	0.63	4.5	−3.209	0.64	1.5	−2.598	0.64	4.5
5	0.15	−2.408	0.53	19.7	−2.765	0.56	13.8	−2.345	0.58	13.4
6	0.18	−2.287	0.50	24.2	−2.733	0.55	15.4	−2.336	0.58	13.4

[a] The reference σ is from Model 2 in Zhou's experiment [3].

show that in DDRM measurement choosing the retraction scale is very important. In the case of large scale retraction $D_0 > 0.2$, use of the shape parameter D is likely to make serious deviation in the measurement, however, the other two shape parameters lead to acceptable measures for the models with small distortions. This study found that the retraction scale $D_0 \cong 0.15$ is the most suitable scale in DDRM measurement. In the scale, the three shape parameters cannot make much difference on the measurement deviation from the standard. This study also found that the distortion criterion γ varies with different shape parameters. In the preceding paper, we found $\gamma < 0.3$ is good for using $(a^2 - b^2)$, which was proved again in present study. It is in the retraction scale $D_0 > 0.2$. We also found here in the most suitable scale $D_0 \cong 0.15$ the distortion criterion $\gamma < 0.15$.

Acknowledgements

The authors are very grateful to Professor Chixing Zhou and Dr Wei Yu for their helpful discussion in the theory of measuring interfacial tension and also acknowledge the financial support from National Natural Science Foundation of China (including 20490220), 863 Project and 973 (G1999064807) Project.

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