

Influence of Different Alkyl Side Chains on Solid Surface Tension of Polymethacrylates

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ABSTRACT: Low-rate dynamic contact angles on poly(*t*-butyl methacrylate) (PtBMA) were measured by an automated axisymmetric drop shape analysis profile (ADSA-P). The solid surface tension of PtBMA is calculated to be 18.1 mJ/m², with a 95% confidence limit of ± 0.6 mJ/m². This value was compared to previous results with different homopolymeric polymethacrylates [poly(methyl methacrylate) (PMMA), poly(ethyl methacrylate) (PEMA), and poly(*n*-butyl methacrylate) (PnBMA)] and with copolymeric polymethacrylates [poly(methyl methacrylate/ethyl methacrylate, 30/70) [P(MMA/EMA, 30/70)] and poly(methyl methacrylate/*n*-butyl methacrylate) [P(MMA/nBMA)]]. It was found that increasing length and size of the alkyl side chain decrease the solid surface tension, as expected. Comparison with pure alkyl surfaces suggests that the surface tension of PtBMA is dominated by the very hydrophobic *t*-butyl group.
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Key words: contact angle; surface tension; polymethacrylates

INTRODUCTION

The surface tension of solid polymers is an important thermodynamic parameter, which plays a decisive role in wetting and adhesion. In a number of technical applications, it is desirable to alter these surface properties. Surface treatments, such as plasma modifications and exposure to flames, or chemical bulk modifications are two main strategies to change the solid surface tension.¹ However, there is a lack of systematic investigations of the relation between the chemi-

cal structure of polymers and their surface energetic properties.

In a previous study, based on contact-angle measurements, we used poly(4-*X*-styrene) to investigate systematically the influence of different substituents [X = H, CH₃, (CH₃)₃, Cl, OH] on the solid surface tension of these materials.² A pronounced effect of the substituents on the surface energetic properties of the respective polymers was found. It was shown that the CH₃ group in poly(4-methylstyrene) causes a decrease of the solid surface tension from 28.3 mJ/m² (polystyrene) to 25.8 mJ/m². This effect was even more pronounced in the case of the voluminous C(CH₃)₃ group in poly(4-*tert*-butylstyrene); a decrease of γ_{sv} to 22.0 mJ/m² was found. These findings are in good agreement with the expectation that the surface tension decreases with increasing size of the alkyl groups.

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In this study, we proposed to consider polymethacrylates which are widely used technical polymers. The materials studied possess the same (polar) polymer backbone, but varying length and size of (nonpolar) alkyl side chains. The question arises whether the surface tension of these polymers reflects the systematic change in the bulk structure. The old literature contains critical surface tension values for polymethacrylates with different alkyl side chains.^{3–6} These data point in the same direction as do the newer data. However, they are of unknown reliability, since it has become apparent more recently that many liquids are, from the point of view of contact-angle measurements, incompatible with specific polymers.^{7,8} Therefore, the older values will not be considered further here. Principles and complications of contact-angle measurements are briefly outlined below.

At the center of contact-angle research is Young's equation,

$$\gamma_{lv} \cos \theta_Y = \gamma_{sv} - \gamma_{sl} \quad (1)$$

which interrelates the Young contact angle θ_Y with the interfacial tensions of the liquid–vapor γ_{lv} , solid–vapor γ_{sv} , and solid–liquid γ_{sl} interfaces. The apparent simplicity of this equation is misleading. In practice, difficulties arise, since the basic assumptions implied in Young's equation (i.e., the presence of a single, unique contact angle and constancy of γ_{lv} , γ_{sv} , and γ_{sl}) are often violated. For example, nearly all solid surfaces exhibit contact-angle hysteresis (difference between advancing contact angle θ_a and receding contact angle θ_r). This leads to the question of which of the experimentally obtained contact angles represents the Young contact angle θ_Y . Based on thermodynamic arguments, it was shown that on smooth, but chemically heterogeneous, solid surfaces the advancing contact angle θ_a is a good approximation of θ_Y ,^{9–11} while no such equality exists on rough solid surfaces. In the case of rough surfaces, the advancing angle θ_a does not reflect only material properties of the surface; rather, it reflects morphological ones as well. Thus, all contact angles on rough surfaces are meaningless in terms of Young's equation. Further complications can be due to interactions between the liquid and the solid, like swelling, penetration, dissolution, or stick/slip behavior. This would lead to nonconstant contact angles and/or interfacial tensions (γ_{lv} , γ_{sv} , and/or γ_{sl}). Therefore, Young's equation would

not be applicable. Using conventional goniometer techniques, these interactions are usually not detectable.⁷ However, it was shown recently^{12–14} that measuring contact angles at a very slow motion of the three-phase contact line allows direct observation of surface quality. In addition, when such procedures are performed by an automated axisymmetric drop shape analysis profile (ADSA-P), complications like those described above can be identified.^{7,15–21} A more complete discussion of the complexity of contact-angle measurements is available in the literature.⁸

In this study, low-rate dynamic contact angles on poly(*t*-butyl methacrylate) (PtBMA) are reported. The results are found to be in harmony with the equation-of-state approach for solid–liquid interfacial tensions,²² which was used to calculate the solid surface tension. The data are compared to previous results for similar homopolymeric polymethacrylates, [poly(methyl methacrylate) (PMMA),¹⁷ poly(ethyl methacrylate) (PEMA),¹⁸ and poly(*n*-butyl methacrylate) (PnBMA)¹⁹] and to copolymeric polymethacrylates [poly(methyl methacrylate/ethyl methacrylate) [P(MMA/EMA, 30/70)]²⁰ and poly(methyl methacrylate/*n*-butyl methacrylate) [P(MMA/*n*-BMA)].²¹ The studies were also performed using ADSA-P. The discussion is in terms of the relationship between the molecular structure and the exposure of molecular groups at the surface and the effect on the surface tension of the polymers.

EXPERIMENTAL

Materials

PtBMA was purchased from Polysciences (Warrington, PA; cat #07037). The chemical formula of all homopolymeric polymethacrylates are given in Figure 1. A 2% PtBMA/chloroform solution was prepared using chloroform (Sigma–Aldrich, Oakville, Canada, 99+% A.C.C. HPLC grade) as the solvent. Silicon wafers + 100, (Silicon Sense, Nashua, NH; thickness: $525 \pm 50 \mu\text{m}$) were selected as the substrate for contact-angle measurements. They were obtained as circular discs of about 10-cm diameter and were cut into rectangular shapes of about $2.5 \times 5 \text{ cm}$. Each rectangular wafer was then soaked in chromic acid for at least 24 h, rinsed with doubly distilled water, and dried under a heat lamp before polymer coating.

The PtBMA-coated surfaces were prepared by a solvent-casting technique: A few drops of the

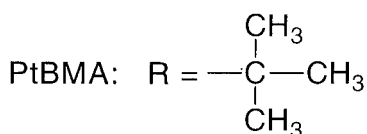
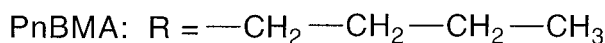
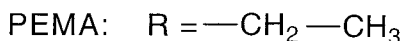
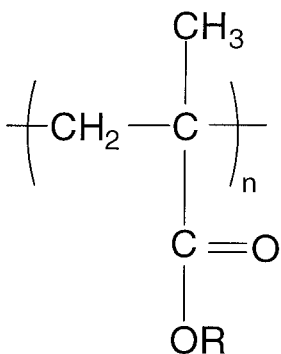


Figure 1 Chemical formulas of PMMA, PEMA, PnBMA, and PtBMA.

PtBMA/chloroform solution were deposited on dry silicon wafers which were then kept inside glass dishes overnight; the solution spread and a thin layer of PtBMA formed on the wafer surface after the chloroform evaporated. This preparation produced smooth coated surfaces, as manifested by light fringes due to refraction at these surfaces, suggesting that surface roughness is in the order of nanometers or less.

Seven liquids were chosen in this study. Water was deionized, doubly distilled, and checked for correct surface tension. The other liquids were used as received. The liquids are listed in Table I, together with the physical properties and surface tensions (measured at $23.0 \pm 0.5^\circ\text{C}$). The surface tensions were independently measured by applying ADSA-P (see below) to a pendent drop. It has been found that, since ADSA assumes an axisymmetric drop shape, the values of the liquid surface tension measured from sessile drops are very sensitive to even a very small amount of surface imperfection, such as roughness and heterogeneity. Hence, γ_{lv} values from pendent drop experiments are more reliable than those from sessile drops.

Methods and Procedures

The ADSA-P is a technique to determine liquid-fluid interfacial tensions and contact angles from the shape of axisymmetric menisci, that is, from sessile as well as pendent drops. The strategy employed is to fit the shape of an experimental drop to a theoretical drop profile according to the Laplace equation of capillarity, using surface/interfacial tension as an adjustable parameter. The best fit identifies the correct surface/interfacial tension and the contact angle. Details of the methodology and experimental setup can be found elsewhere.^{23–27}

With respect to the low-rate dynamic contact-angle measurements by ADSA-P, liquid is supplied to the sessile drop from below the solid surface using a motorized syringe device. It is a good strategy^{28,29} first to deposit a small drop of liquid on a given solid surface covering the small hole, which is needed to supply liquid from below. This experimental procedure, which avoids contact of a capillary with the drop from above, is necessary

Table I Supplier, Purity, and Surface Tension of the Liquids Used

Liquid	Supplier	% Purity	Density (g/cm ³)	γ_{lv} (mJ/m ²)	No. Drops
Water	LAST ^a	Doubly distilled	0.977	72.70 ± 0.09	10
Glycerol	Baker-analyzed ^b	99.8	1.258	65.02 ± 0.04	8
Formamide	Aldrich ^c	99.5+	1.134	59.08 ± 0.04	10
Ethylene glycol	Aldrich ^c	99+	1.113	48.66 ± 0.06	10
3-Pyridylcarbinol	Aldrich ^c	98	1.124	47.81 ± 0.03	10
Diethylene glycol	Aldrich ^c	99	1.118	44.68 ± 0.03	9
1-Bromonaphthalene	Aldrich ^c	98	1.489	44.31 ± 0.05	7

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^b Phillipsburg, NY.

^c Oakville, Canada.

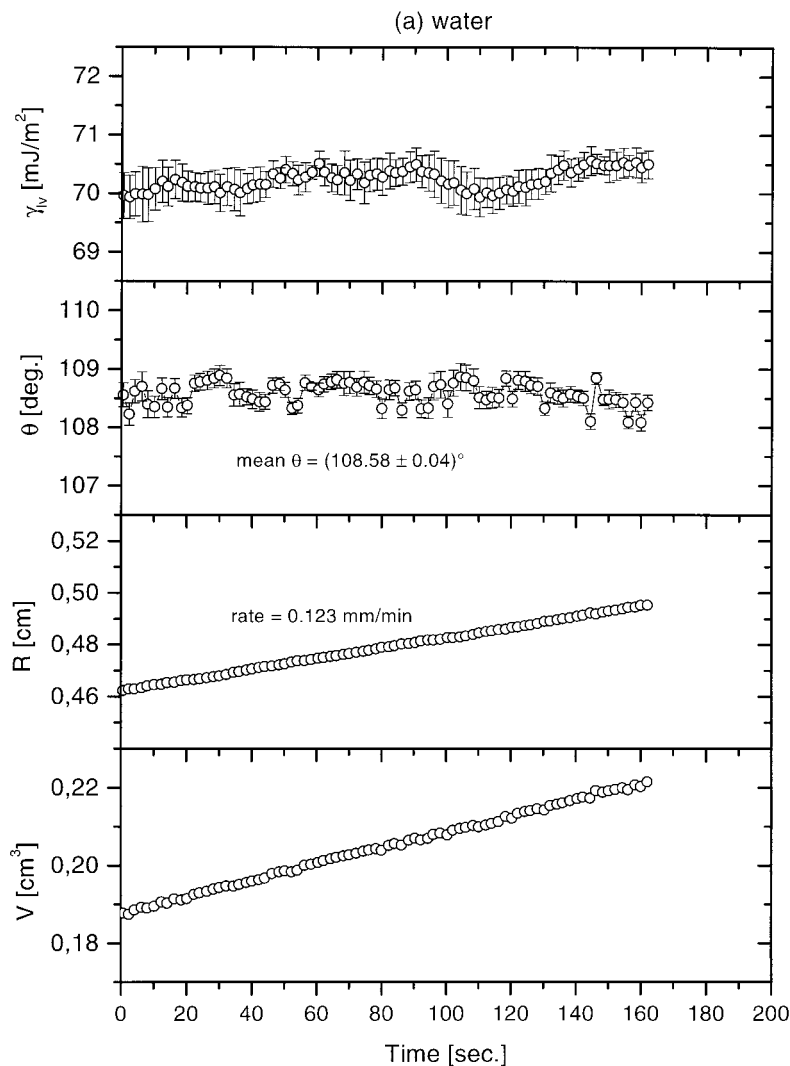


Figure 2 Low-rate dynamic contact angles of (a) water, (b) glycerol, (c) formamide, (d) ethylene glycol, and (e) diethylene glycol on PtBMA; γ_{lv} , θ , R , and V are, respectively, the liquid–vapor surface tension, contact angle, radius of the three-phase contact line, and drop volume.

since ADSA determines the contact angles based on a complete and undisturbed drop profile.

While the drop is growing at very slow motion of the three-phase contact line, a sequence of images is recorded by the computer (typically one image every 2–5 s). Since ADSA-P determines the contact angle and the three-phase contact radius simultaneously for each image, the advancing dynamic contact angle can be obtained as a function of the three-phase contact radius (i.e., location on the surface). Furthermore, the liquid surface tension is determined for each image and can also be recorded. If the polymer surface is not very smooth or other complexities due to swelling,

stick/slip, etc., occur, irregular and inconsistent contact angle or liquid surface tension values will be seen as the drop grows. Hence, contact angles, which are meaningless for the calculation of solid surface tensions, can be identified and disregarded. Conventional goniometric techniques provide only the contact angle as output information and are therefore not capable of distinguishing between meaningful and meaningless contact angles. Details of the procedure and the experimental setup for low-rate dynamic contact-angle measurements are given elsewhere.^{2,7,12,14–21,23}

At least six dynamic contact-angle measurements at velocities of the three-phase contact

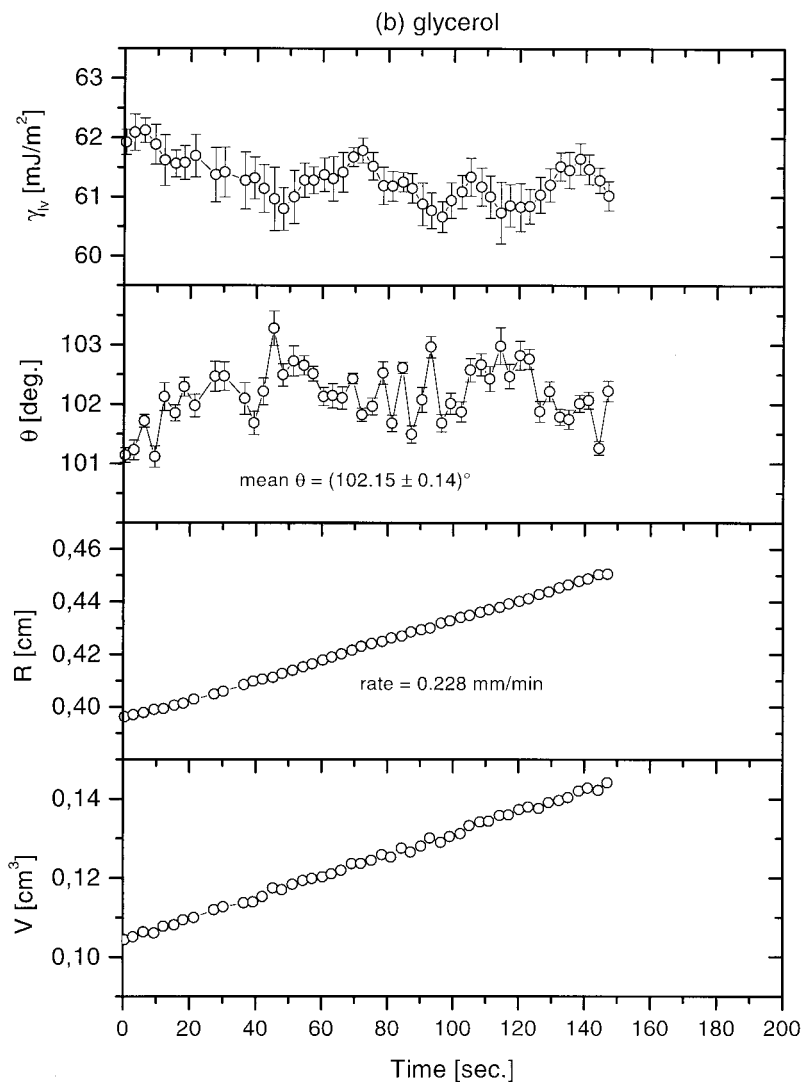


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line in the range of 0.07–0.28 mm/min were performed for each liquid. The choice of this velocity range was based on previous studies^{7,12–14} which showed that low-rate dynamic contact angles at these velocities are essentially identical with the static contact angles for these relatively smooth surfaces. When the measured contact angles are essentially constant at different surface locations, the mean contact angle for a specific rate of advancing can be obtained by averaging the contact angles, after the three-phase contact radius reaches 0.4–0.5 cm. The purpose of choosing these relatively large drops is to avoid any line tension effects on the measured contact angles.^{30,31} During the experiments, the temperature and relative humidity

were maintained, respectively, at $23 \pm 0.5^\circ\text{C}$ and about 40%.

RESULTS AND DISCUSSION

Of the seven liquids used, it was found that two liquids yielded nonconstant contact angles during the course of the experiments: 1-Bromonaphthalene dissolved the polymer on contact, and in the case of 3-pyridylcarbinol, the contact angle decreased continuously from 78° to about 74° , presumably due to a sorption process, while the drop was smoothly advancing on the PtBMA surface. The remaining five liquids yielded usable contact angles.

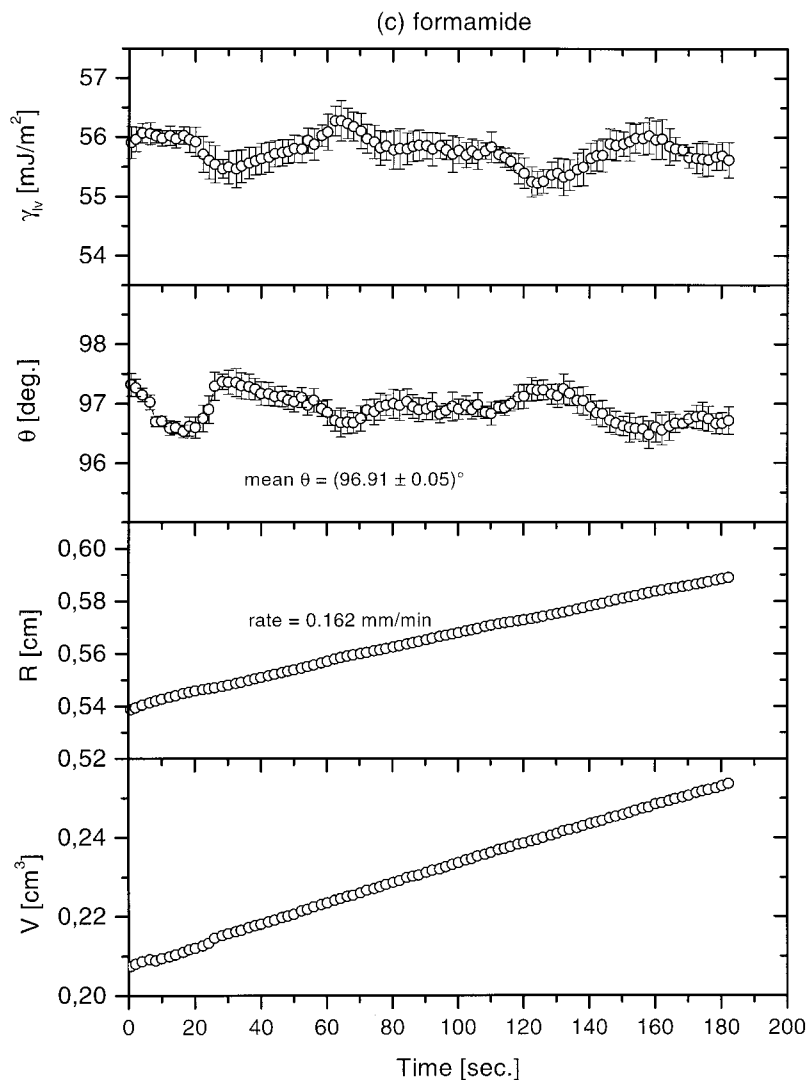


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Figure 2(a–e) shows, respectively, typical experimental results of water, glycerol, formamide, ethylene glycol, and diethylene glycol. As can be seen in the figures, the contact angles are essentially constant, as the drop volume V and, hence, the three-phase contact radius R increases. This constancy of the contact angles with increasing contact radius R indicates independence of the location on the surface and of time and suggests that the contact angle is a Young contact angle. The minor variation of such angles observable in the figures cannot even be detected by conventional goniometric techniques, which have $\pm 2^\circ$ accuracy. Increasing the drop volume in this manner ensures that the measured contact angle θ is an advancing contact angle. It should be noted that the liquid–vapor surface tension values cal-

culated by ADSA-P for these sessile drops are fairly constant, but not as reliable as those from pendent drops, as explained above. The accuracy depends on strict axisymmetry of the drop profile, and this is easier to achieve with pendent drops.

The reproducibility of all solid–liquid systems is very good. The results are summarized in Table II for the five liquids with usable contact angles, at different rates of advancing. Each measurement was performed on a newly prepared surface. For instance, in the specific case of water in Table II, a final value of $\theta = 108.08^\circ \pm 0.53^\circ$ was obtained, by averaging the contact angles for seven different experiments. The 95% confidence limits calculated in this manner (in Table II) include all possible errors, due to experimental technique, solid surface preparation, etc.

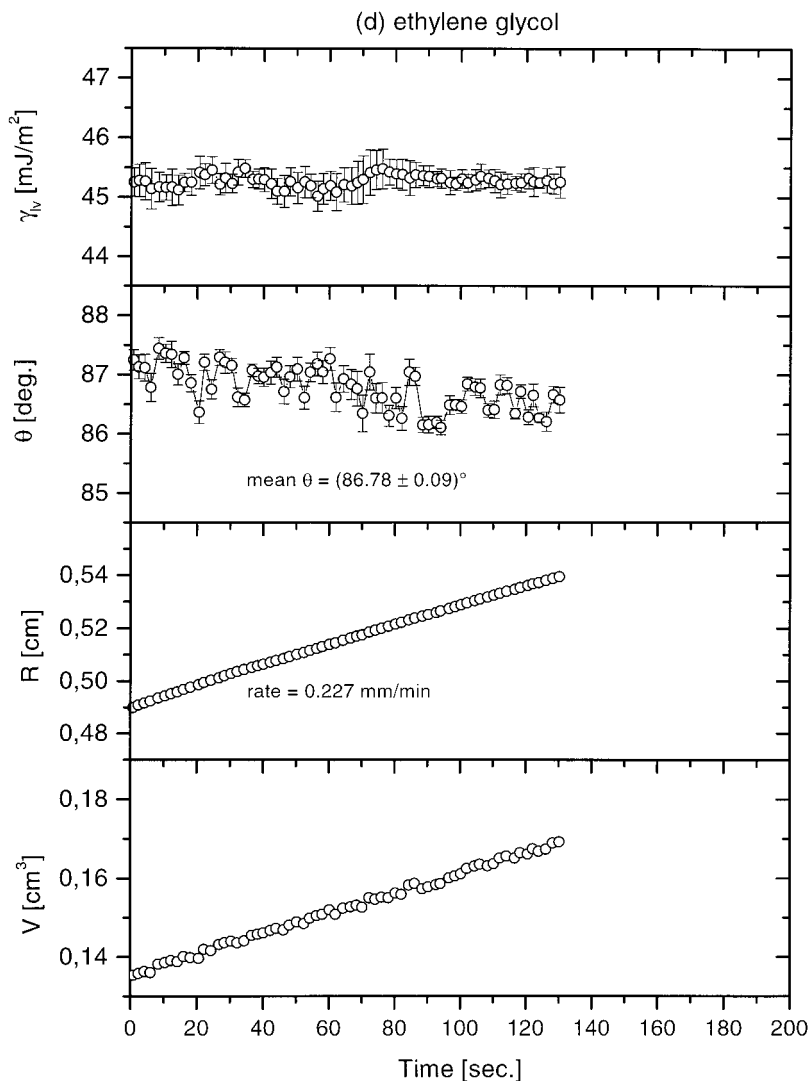


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In Figure 3, the contact-angle results from Table II are plotted as $\gamma_{lv}\cos\theta$ versus γ_{lv} , together with the error limits calculated from the contact-angle errors. It can be seen that all liquids fall on a smooth curve, that is, the values of $\gamma_{lv}\cos\theta$ for a given solid (i.e., constant γ_{sv}) change smoothly with γ_{lv} . This is in agreement with the patterns reported by Li et al.^{32,33} and Kwok et al.^{7,12,14–21} for a large number of diverse polar and nonpolar (noninert and inert) polymer surfaces. Thus, again, it can be concluded that

$$\gamma_{lv}\cos\theta = F(\gamma_{lv}, \gamma_{sv}) \quad (2)$$

and, hence, because of Young's equation,

$$\gamma_{sl} = f(\gamma_{lv}, \gamma_{sv}) \quad (3)$$

In Figure 4, the contact-angle data from Pt-BMA are compared with previous results for other homopolymeric polymethacrylates (PMMA,¹⁷ PEMA,¹⁸ and PnBMA¹⁹) and to a copolymeric polymethacrylate, P(MMA/EMA, 30/70).²⁰ Again, for each polymer, the values of $\gamma_{lv}\cos\theta$ change smoothly with γ_{lv} . Furthermore, it can be seen that varying the length and size of the alkyl side chains shifts the curves in a regular and expected manner: The polar ester groups of the polymer backbone produce a fairly hydrophilic surface. As the size of the hydrophobic alkyl substituent (R) is increased, the effect of the ester groups is reduced and, therefore, the material becomes more

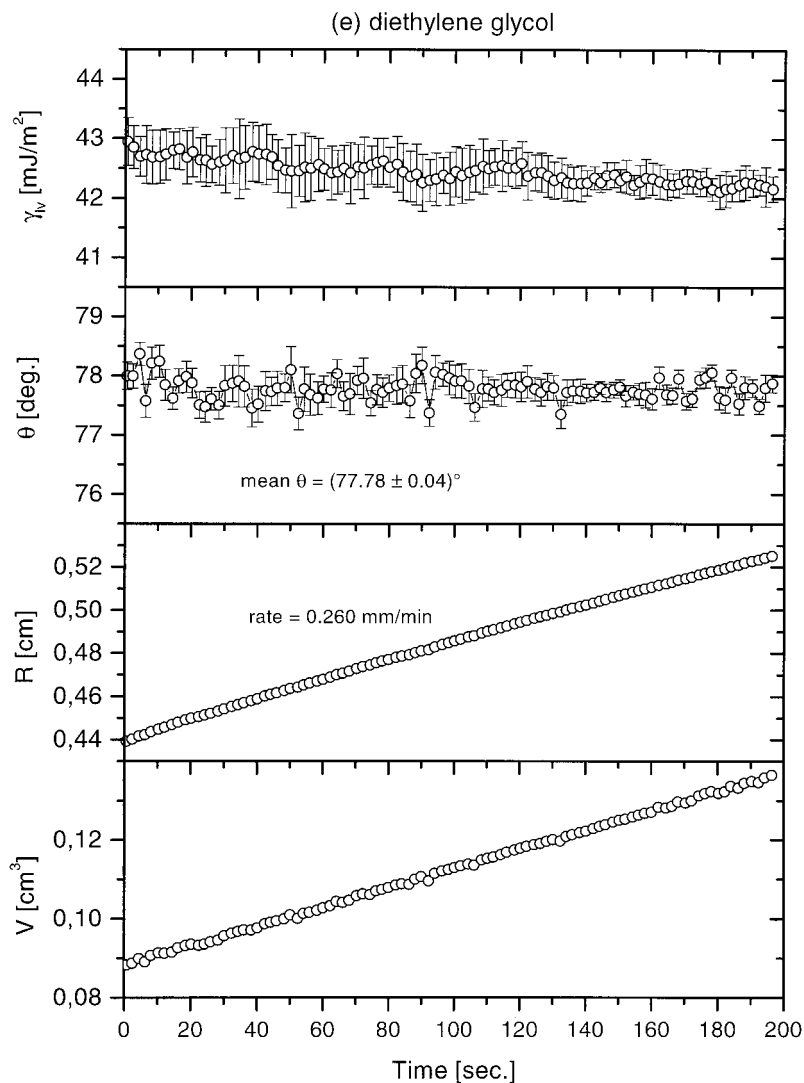


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hydrophobic. Thus, for the same liquid, larger contact angles are obtained, and the curves are shifted toward the bottom of the graph. In addition, Figure 4 shows that the curve of the P(MMA/EMA, 30/70) copolymer, which contains a mixture of methyl and ethyl side chains, falls between the corresponding homopolymeric polymethacrylates PMMA and PEMA. It is somewhat closer to the PEMA curve, due to the higher content of ethyl groups.

The effect of the different alkyl side chains can be further elucidated by calculating the solid surface tensions of the polymethacrylates. On phenomenological grounds, an equation-of-state approach for solid-liquid interfacial tensions, that is, an explicit expression of eq. (3), was formulated²²:

$$\gamma_{sl} = \gamma_{lv} + \gamma_{sv} - 2\sqrt{\gamma_{lv}\gamma_{sv}}e^{-\beta(\gamma_{lv}-\gamma_{sv})^2} \quad (4)$$

where β is a constant, which was found to be $0.0001247 \text{ (m}^2/\text{mJ)}^2$. Combining this equation with Young's equation yields

$$\cos \theta_Y = -1 + 2\sqrt{\frac{\gamma_{sv}}{\gamma_{lv}}}e^{-\beta(\gamma_{lv}-\gamma_{sv})^2} \quad (5)$$

Thus, solid surface tensions can be calculated from experimental (Young) contact angles and liquid surface tensions.

For PtBMA, the solid surface tensions calculated for the different liquids are summarized in Table III. The values are quite constant, essen-

Table II Summary of the Contact Angles (degree) at Different Rates (mm/min) of Motion of the Three-phase Contact Line for Liquids Which Yielded Constant Contact Angles on a PtBMA-coated Silicon Wafer

Water		Glycerol		Formamide	
Rate	θ	Rate	θ	Rate	θ
0.074	108.50 ± 0.17	0.129	100.36 ± 0.06	0.119	97.18 ± 0.14
0.113	108.82 ± 0.03	0.134	102.04 ± 0.06	0.150	96.48 ± 0.05
0.123	108.58 ± 0.04	0.137	100.95 ± 0.04	0.157	96.43 ± 0.06
0.125	107.35 ± 0.03	0.147	101.53 ± 0.04	0.159	96.48 ± 0.04
0.151	107.85 ± 0.06	0.187	102.44 ± 0.08	0.161	96.15 ± 0.07
0.170	107.42 ± 0.09	0.201	101.95 ± 0.08	0.162	96.65 ± 0.05
0.172	108.05 ± 0.07	0.203	102.67 ± 0.35	0.162	96.91 ± 0.05
		0.206	101.67 ± 0.10	0.165	97.42 ± 0.08
		0.206	102.63 ± 0.12	0.166	95.82 ± 0.08
		0.208	101.23 ± 0.15	0.174	95.56 ± 0.04
		0.212	102.69 ± 0.13	0.188	96.94 ± 0.16
		0.228	102.15 ± 0.14		
		0.256	101.86 ± 0.11		
	108.08 ± 0.53 ^a		101.86 ± 0.43 ^a		96.55 ± 0.38 ^a
Ethylene Glycol		Diethylene Glycol			
Rate	θ	Rate	θ		
0.167	84.65 ± 0.06	0.202	78.62 ± 0.07		
0.203	86.46 ± 0.08	0.219	77.54 ± 0.04		
0.216	85.77 ± 0.05	0.230	78.63 ± 0.08		
0.223	85.74 ± 0.05	0.235	79.51 ± 0.07		
0.227	86.78 ± 0.09	0.260	77.78 ± 0.04		
0.228	85.85 ± 0.09	0.281	78.91 ± 0.08		
0.230	85.04 ± 0.09				
0.247	86.00 ± 0.17				
	85.79 ± 0.58 ^a		78.50 ± 0.77 ^a		

^a Mean θ value with the 95% confidence limits.

tially independent of the liquids used. In the case of diethylene glycol, the calculated γ_{sv} value is about 1 mJ/m² higher compared to the other liquids. As can be seen from Figures 3 and 4, the contact angle of this liquid shows a slight deviation from the smooth curve, which is somewhat outside the error limits of the ADSA measurements. Similar deviations of contact-angle data also appear for the other polymethacrylates (see Fig. 4). The question whether these deviations are artifacts or whether they reflect physical reality needs further study. The mean γ_{sv} value of PtBMA was found to be 18.1 mJ/m² with a 95% confidence limit of ±0.6 mJ/m².

In Table IV, the surface tension of PtBMA is compared to the previous results of the different

homo- and copolymeric polymethacrylates. Also included are the values of another copolymer, P(MMA/nBMA),²¹ with an unknown ratio of the two comonomers, and, as reference, poly(4-*t*-butylstyrene),² hexatriacontane, and siliconized glass.¹⁰ PMMA has the largest surface tension (38.5 mJ/m²), followed by P(MMA/EMA, 30/70) (35.1 mJ/m²), PEMA (33.6 mJ/m²), and PnBMA (28.8 mJ/m²); PtBMA has the lowest value (18.1 mJ/m²). These values reflect the trend expressed by the shift of the curves in the $\gamma_{lv} \cos \theta$ versus γ_{lv} diagram (Fig. 4). It appears that the polar polyester backbone is shielded by the alkyl side chains and its influence on the surface tension of the polymethacrylates diminishes as the length and size of the substituents

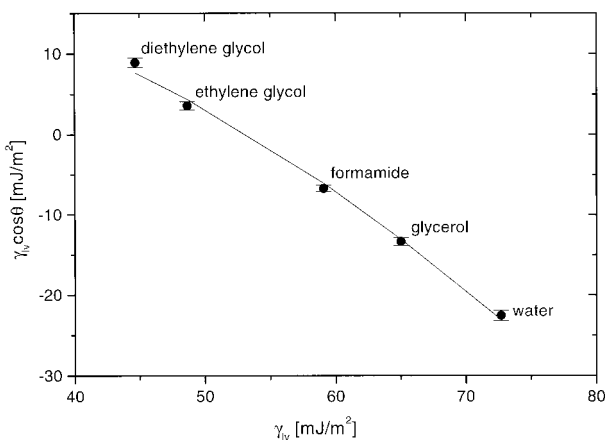


Figure 3 Values of $\gamma_{lv}\cos\theta$ versus γ_{lv} for the PtBMA-coated wafer surface for the data in Table II.

increases. It is of interest to discuss this effect in more detail:

We can compare the surface tension of the P(MMA/EMA, 30/70) copolymer with the values of PMMA and PEMA. If we would estimate the surface tension of the copolymer from the values of the pure homopolymers, taking into account the ratio of methyl (30%) to ethyl groups (70%), we would end up with a value of 35.1 mJ/m^2 . This agrees remarkably well with the experimental surface tension of P(MMA/EMA, 30/70), which

was found to have exactly the same value, that is, the difference in the “shielding ability” of the methyl and ethyl groups adds up linearly to an intermediate value for the copolymer, so that the ratio of the two alkyl side chains is reflected directly by the solid surface tension. Another copolymeric methacrylate that was studied is P(MMA/nBMA).²¹ For this material, the ratio of the two comonomers is not known. However, by comparing its surface tension with the values of PMMA and PnBMA, we can estimate the ratio in the 50 : 50 range, possibly with a slightly higher content of methyl groups. A direct observation of the surface composition (e.g., with XPS) would be desirable, but this is beyond the scope of this article.

Comparison of the results of the homopolymers with linear alkyl side chains (PMMA, PEMA, and PnBMA) shows that increasing the chain length leads to a nonlinear decrease of solid surface tension. Adding one methylene group (PMMA \rightarrow PEMA) reduces the surface tension by 5 mJ/m^2 . Going to PnBMA, the surface tension is reduced by another 5 mJ/m^2 , but in this case, two methylene groups were added, that is, with increasing chain length of the alkyl substituent, the capability of reducing the solid surface tension is less pronounced. Based on this finding, it has to be expected that increasing the length further

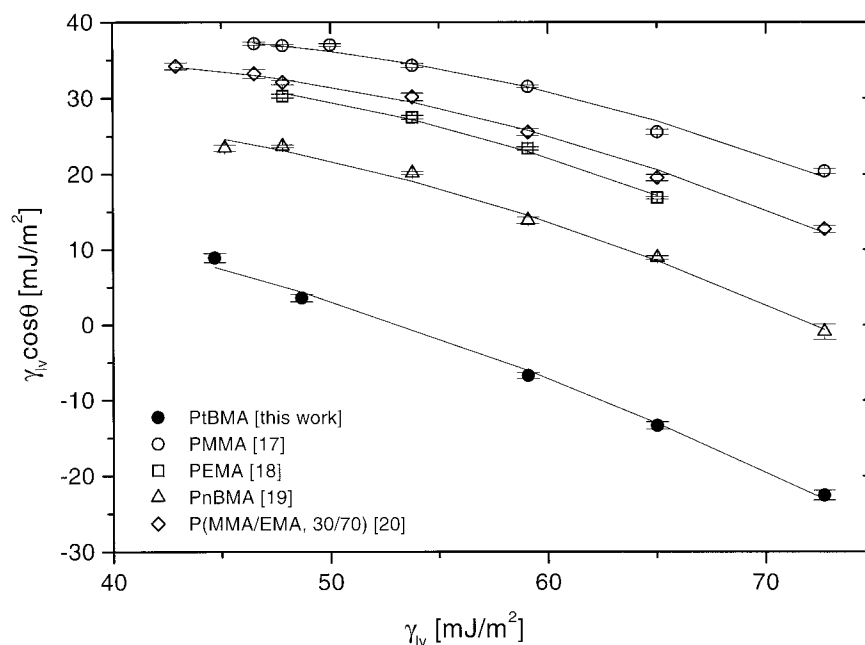


Figure 4 Values of $\gamma_{lv}\cos\theta$ versus γ_{lv} for PMMA-, P(MMA/EMA, 30/70)-, PEMA-, PnBMA-, and PtBMA-coated wafer surfaces.

Table III Solid-surface Tension Values, γ_{sv} , of a PtBMA-coated Silicon Wafer, Calculated from the Equation-of-state Approach for Solid-Liquid Interfacial Tensions²²

Liquids	γ_{lv} (mJ/m ²)	θ (degree)	γ_{sv} (mJ/m ²)
Water	72.70 ± 0.09 ^a	108.08 ± 0.53 ^a	18.2 ± 0.4 ^b
Glycerol	65.02 ± 0.04 ^a	101.86 ± 0.43 ^a	17.9 ± 0.3 ^b
Formamide	59.08 ± 0.04 ^a	96.55 ± 0.38 ^a	17.8 ± 0.3 ^b
Ethylene glycol	48.66 ± 0.06 ^a	85.79 ± 0.58 ^a	17.8 ± 0.3 ^b
Diethylene glycol	44.68 ± 0.03 ^a	78.50 ± 0.77 ^a	19.0 ± 0.4 ^b
Mean value			18.1 ± 0.6 ^a

^a Errors are 95% confidence limits.

^b Errors are estimated from the errors of γ_{lv} and θ by inserting the minimum γ_{lv} value together with the maximum θ value (or vice versa, respectively) into eq. (5).

should lead to a limiting value of the solid surface tension. The interesting question that arises is how many methylene groups are needed to reach that point. A plausible limiting value would be the surface tension of polyethylene. Unfortunately, there are no contact angle data available yet that meet the high-quality standard of the ADSA-P methodology. As already stated, measurements by a simple goniometer technique led to a mixture of meaningful and meaningless contact angles in terms of surface energetics. However, based on literature values of unknown reliability, the surface tension of polyethylene can be estimated to lie somewhere between 25 and 30 mJ/m².³⁴ This is in the same order of magnitude as is the surface tension of PnBMA (28.8 mJ/m²), that is, the surface tension of PnBMA is close to the expected limiting value. Longer alkyl side chains than *n*-butyl (e.g., *n*-hexyl and *n*-octyl)

should not decrease the surface tension of the polymethacrylates significantly.

The *tert*-butyl substituent of PtBMA is much bulkier than are the linear alkyl side chains. Therefore, its ability to “shield” the polar backbone should be more pronounced, which is reflected by the very low surface tension of only 18.1 mJ/m². It is informative to compare this value to the data of pure alkyl surfaces, like that of hexatriacontane (20.4 mJ/m²) and siliconized glass (18.2 mJ/m²). It is known that these surfaces consist only of methyl groups.¹⁰ Since the surface tension of PtBMA is in the same range, it can be concluded that its surface should consist predominantly of the bulky *t*-butyl substituent and that the ester group has no significant influence on the solid surface tension. Hence, the maximum thickness of the top surface layer, to which the contact angle is sensitive, can be estimated to have approximately the size of the *t*-butyl group (i.e., about 2.6 Å). This well-known fact of the dominance of the top molecular groups is further supported by the data from another *t*-butyl-modified polymer: For poly(4-*t*-butylstyrene), a surface tension of 22.0 mJ/m² was obtained,² which falls in the same range, suggesting that the contact angle is only sensitive to the bulky *t*-butyl substituent, regardless of the polymer backbone. It is believed that the small differences between PtBMA, poly(4-*t*-butylstyrene), hexatriacontane, and silicone oil are essentially due to different packing of the methyl groups.

CONCLUSIONS

The solid surface tension of PtBMA was found to be 18.1 ± 0.6 mJ/m². This value, which at first

Table IV Solid-surface Tension Values, γ_{sv} , Calculated from the Equation-of-state Approach for Solid-Liquid Interfacial Tensions²²

Polymer	γ_{sv} (mJ/m ²)
PMMA ¹⁷	38.5 ± 0.5
PEMA ¹⁸	33.6 ± 0.5
PnBMA ¹⁹	28.8 ± 0.5
PtBMA (this work)	18.1 ± 0.6
P(MMA/EMA, 30/70) ²⁰	35.1 ± 0.3
P(MMA/nBMA) ²¹	34.4 ± 0.8
Poly(4- <i>t</i> -Butylstyrene) ²	22.0
Hexatriacontane ¹⁰	20.4 ± 0.2 ^a
Siliconized glass ¹⁰	18.2 ± 0.1 ^a

^a At 20°C.

sight seems to be surprisingly low, becomes entirely plausible when it is compared with previous results of other polymethacrylates with different alkyl side chains. As expected, it was found that the solid surface tension decreases with increasing length and size of the alkyl substituents. The *t*-butyl group is the bulkiest of the alkyl groups considered and, therefore, PtBMA has the lowest surface tension. This low value is comparable to that of surfaces which consist only of methyl groups. Thus, it was concluded that the surface properties of PtBMA are governed by the *t*-butyl group.

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REFERENCES

- Grundke, K.; Jacobasch, H.-J.; Simon, F.; Schneider, S. *J Adhes Sci Technol* 1995, 9, 327.
- Augsburg, A.; Grundke, K.; Poeschel, K.; Jacobasch, H.-J.; Neumann, A. W. *Acta Polym* 1998, 49, 417.
- Zisman, W. A. In *Advances in Chemistry Series 43*; American Chemical Society: Washington, DC, 1964.
- Wu, S. *Org Coat Plast Chem* 1971, 31, 27.
- Kamagata, K.; Toyama, M. *J Appl Polym Sci* 1974, 18, 167.
- Toyama, M.; Watanabe, A.; Ito, T. *J Colloid Interface Sci* 1974, 47, 802.
- Kwok, D. Y.; Gietzelt, T.; Grundke, K.; Jacobasch, H.-J.; Neumann, A. W. *Langmuir* 1997, 13, 2880.
- Kwok, D. Y.; Neumann, A. W. *Adv Colloid Interface Sci* 1999, 81, 167.
- Johnson, R. E.; Dettre, R. H. *J Phys Chem* 1964, 68, 1744.
- Neumann, A. W. *Adv Colloid Interface Sci* 1974, 4, 105.
- Li, D.; Neumann, A. W. In *Applied Surface Thermodynamics*; Neumann, A. W.; Spelt, J. K., Eds.; Marcel Dekker: New York, 1996; pp 109–168.
- Kwok, D. Y.; Lin, R.; Mui, M.; Neuman, A. W. *Colloids Surf A* 1996, 116, 63.
- Kwok, D. Y.; Li, D.; Neumann, A. W. In *Applied Surface Thermodynamics*; Neumann, A. W.; Spelt, J. K., Eds.; Marcel Dekker: New York, 1996; pp 413–440.
- Kwok, D. Y.; Budziak, C. J.; Neumann, A. W. *J Colloid Interface Sci* 1995, 173, 143.
- Kwok, D. Y.; Lam, C. N. C.; Li, A.; Leung, A.; Neumann, A. W. *Langmuir* 1998, 14, 2221.
- Del Rio, O. I.; Kwok, D. Y.; Wu, R.; Alvarez, J. M.; Neumann, A. W. *Colloids Surf A* 1998, 143, 197.
- Kwok, D. Y.; Leung, A.; Lam, C. N. C.; Li, A.; Wu, R.; Neumann, A. W. *J Colloid Interface Sci* 1998, 206, 44.
- Kwok, D. Y.; Wu, R.; Li, A.; Neumann, A. W. *J Adhes Sci Technol*, in press.
- Kwok, D. Y.; Leung, A.; Li, A.; Lam, C. N. C.; Wu, R.; Neumann, A. W. *Colloid Polym Sci* 1998, 276, 459.
- Kwok, D. Y.; Li, A.; Neumann, A. W. *J Polym Sci B* 1999, 37, 2039.
- Kwok, D. Y.; Lam, C. N. C.; Li, A.; Neumann, A. W. *J Adhes* 1998, 68, 229.
- Spelt, J. K.; Li, D. In *Applied Surface Thermodynamics*; Neumann, A. W.; Spelt, J. K., Eds.; Marcel Dekker: New York, 1996; pp 239–292.
- Kwok, D. Y.; Lam, C. N. C.; Li, A.; Zhu, K.; Wu, R.; Neumann, A. W. *Polym Eng Sci* 1998, 38, 1675.
- Rotenberg, Y.; Boruvka, L.; Neumann, A. W. *J Colloid Interface Sci* 1983, 93, 169.
- Cheng, P.; Li, D.; Boruvka, L.; Rotenberg, Y.; Neumann, A. W. *Colloids Surf* 1983, 93, 169.
- Lahooti, S.; del Rio, O. I.; Cheng, P.; Neumann, A. W. In *Applied Surface Thermodynamics*; Neumann, A. W.; Spelt, J. K., Eds.; Marcel Dekker: New York, 1996; pp 441–507.
- Del Rio, O. I.; Neumann, A. W. *J Colloid Interface Sci* 1997, 196, 136.
- Oliver, J. F.; Huh, C.; Mason, S. G. *J Colloid Interface Sci* 1977, 59, 568.
- Oliver, J. F.; Huh, C.; Mason, S. G. *Colloids Surf* 1980, 1, 79.
- Duncan, D.; Li, D.; Gaydos, J.; Neumann, A. W. *J Colloid Interface Sci* 1995, 169, 256.
- Gaydos, J.; Neumann, A. W. In *Applied Surface Thermodynamics*; Neumann, A. W.; Spelt, J. K., Eds.; Marcel Dekker: New York, 1996; pp 169–238.
- Li, D.; Neumann, A. W. *J Colloid Interface Sci* 1992, 148, 190.
- Li, D.; Xie, M.; Neumann, A. W. *Colloid Polym Sci* 1993, 271, 573.
- Wu, S. *Polymer Interface and Adhesion*; Marcel Dekker: New York, 1982.