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Surface dynamics for poly(vinyl alkylate)s via dynamic contact angle and adhesion tension relaxation

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Dynamic contact angle (DCA) and adhesion tension relaxation (ATR) for poly(vinyl alkylate)s (PVAls) were measured. Advancing contact angle initially increased with an increase in the side-chain-length and after a maximum at C10, it decreased, while receding contact angle showed a complex behaviour. A large contact-angle hysteresis was observed. DCA also depended on the dipping velocity. Results on ATRs showed that the surface molecule of these PVAls had large molecular mobility. Reproducibility of ATR was also observed. These phenomena were explained by the reorientation of the segment at polymer/water or polymer/air interface so as to minimize interfacial free energy. Copyright © 1996 Published by Elsevier Science Ltd.

(Keywords: dynamic contact angle; adhesion tension relaxation; poly(vinyl alkylate))

INTRODUCTION

It is well known that some multicomponent polymeric systems such as copolymers adsorb and orient selectively to the surface of systems so as to minimize interfacial free energy in response to a polarity of an environmental medium. We[1–6] have already reported on this phenomenon via interfacial tension. Recently, a surface molecular mobility of a multi-component polymeric system has been investigated via dynamic contact angle (DCA) measurements. DCA is a useful tool to investigate these phenomena, because a re-orientation of surface segments directly reflects contact angle hysteresis when a polymer is moved into a different medium.

In addition, the re-orientation of an area of polymer surface, resulting in a decrease in interfacial tension is responsible for the variation of adhesion tension ($\gamma_L \cos\theta = \gamma_S - \gamma_{SL}$), depending on elapsed time. The variation can be recognized as a kind of relaxation, because it has arisen by molecular motion when polymer is placed in a different medium. Therefore, we call this phenomenon adhesion tension relaxation (ATR). ATR also can be a useful tool to investigate surface molecular mobility.

The effect of side chains on the property of polymers is an interesting theme in the field of polymer science. It is well known that the glass transition temperature (T_g) of poly(alkyl acrylate)s decreases with an increase in alkyl side chain length, and that after reaching a minimum value at C8, it increases again. We[7] have already reported the surface tension of poly(vinyl alkylate)s (PVAls) in relation to alkyl side chain length. A similar behaviour was shown to a T_g, depending on the alkyl side chain length. In addition to this, we[8] also reported the selective adsorption behaviour of PVAls to water/solvent interfaces from their organic solutions. Here it was shown that the polarity of the polymers, and their solubility to a solvent largely influence their adsorption behaviour.

A number of papers have been published on DCA in relation to side chain length for polymers. Damme and coworkers[9,10] reported on the relationship between the dynamic contact angle for poly(*n*-alkyl methacrylate) and the alkyl side chain length. Chen and Andrade[11] reported the surface characteristics of polysulfoalkyl methacrylates in relation to alkyl side chain length. Takahara *et al.*[14] reported on the surface molecular mobility of copolymers composed of styrene and polyethyleneglycol methacrylates (MPEGMA), which had a different length of polyether pendent segments. We[12,13] reported the DCA of a copolymer composed of methyl methacrylate (MMA) and MPEGMA, terpolymer composed of MMA, MPEGMA, and polydimethylsiloxanemethacrylate (PDMSMA) in relation to polyether and PDMS side chains.

On adhesion tension relaxation, only few papers have been published. Takahara *et al.*[14] reported on adhesion tension relaxation in advancing process for some poly(ether urethane ureas).

In this paper, we discuss the surface molecular mobility of alkyl side chains of PVAls via dynamic contact angle, adhesion tension relaxation and X.p.s. measurements.

EXPERIMENTAL

Materials

For poly(vinyl alkylate)s (PVAls), we used nine kinds

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Table 1 Characterization of poly(vinyl alkylate)s, (PVAls), used

				Atomic ratio (O_{1S}/C_{1S})		
PVAls	Abbr.	M_n	M_w/M_n	Calc.[a]	90°[b]	15°[b]
poly(vinylacetate)	C2	11,000	1.63	0.50	0.50	0.42
poly(vynilbutylate)	C3	17,000	2.07	0.40	0.41	0.38
Poly(vinylbutylate)	C4	19,000	2.41	0.33	0.34	0.33
Poly(vinylcaproate)	C6	21,000	1.95	0.25	0.27	0.27
Poly(vinylcaprylate)	C8	19,000	2.03	0.20	0.20	0.18
Poly(vinylcaprate)	C10	19,000	2.45	0.17	0.18	0.15
Poly(vinyllaurate)	C12	15,000	2.39	0.14	0.15	0.12
Poly(vinylmyristate)	C14	19,000	1.88	0.12	0.08	0.11
Poly(vinylpalmitate)	C16	15,000	2.14	0.11	0.11	0.08
Poly(vinylstearate)	C18	13,000	1.69	0.10	0.09	0.11

[a] Calculated values from molecular structure
[b] Photoelectron take-off angles of sample holder of X.p.s. measurement

of polyvinyl esters with *n*-aliphatic acids which had *n*-alkyl groups with carbon numbers from two to 18. Here we represent an individual PVAl, using such nomenclature as C2, C3, C4 and so on. The number following the C designation represents the number of carbon atoms in the alkyl side chain of the polymer. Polyvinyl acetate (PVC2) was supplied by Nihon Gosei Co. NZ-2. We synthesized the other PVAls from commercially available *n*-alkylate monomers, using *t*-butylperoxy(2-ethylhexanoate) as an initiator. The characteristics of PVAls are listed in *Table 1*.

Preparation of sample plate for DCA measurements

An aluminum plate (20 mm wide, 50 mm length, and 0.3 mm thick) which was rinsed with an ultrasonic washer in trichloroethylene, was coated with the polymers dipping into the solution of PVAl in methyl ethyl ketone (MEK) or toluene. The coated plate was then dried in a vacuum oven at 70°C for more than 10 h.

Dynamic contact angle measurement

For DCA measurement, we employed an instrument made by Orientec Corporation (DCA20), applying the Wilhelmy plate technique, used for measuring the surface tension of a liquid.

In *Figure 1*, the principle of the Wilhelmy method[8] is shown. A sample plate, hanging onto a load cell, is dipped into and out of a standard liquid, giving the contact angle. Condition A shows the plate hanging onto the load cell. The force (F) applied to the load cell can be described as follows

$$F = mg \tag{1}$$

where m is the mass of the plate and g is the acceleration of gravity. Condition B shows the bottom of the plate, just coming into contact with the liquid surface. Here F can be described as follows

$$F = mg + P\gamma_L \cos\theta \tag{2}$$

where P is the perimeter of the plate, γ_L is the surface tension of the liquid, and θ is the contact angle. Condition C shows the plate dipping into the liquid. F can be described as follows

$$F = mg + P\gamma_L \cos\theta - F_b \tag{3}$$

where F_b is the buoyancy.

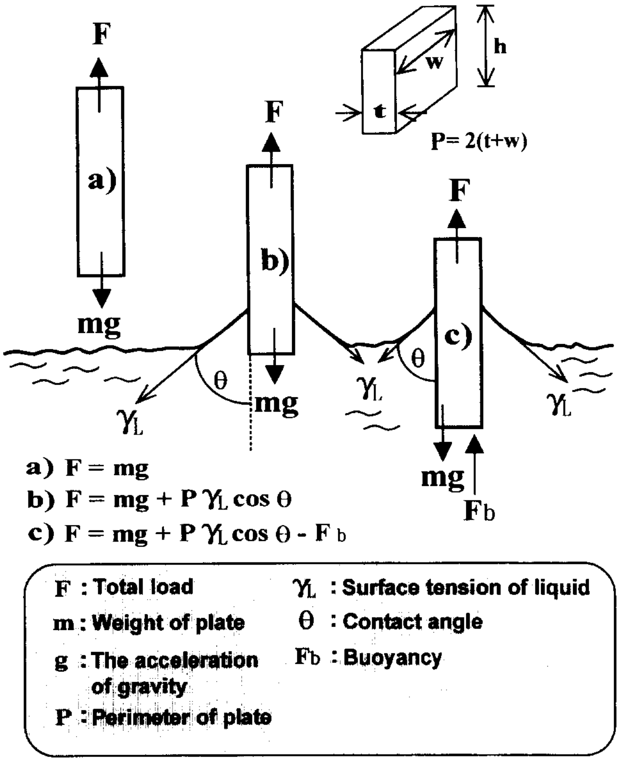

Figure 1 Scheme of principle of dynamic contact angle measurements by the Wilhelmy method

If zero-adjusting of the recorder is performed in condition A, the mass of the plate can be neglected in equation (2). Then F can be described as follows

$$F = P\gamma_L \cos\theta \tag{4}$$

Young's equation is also held, as follows

$$\gamma_L \cos\theta = \gamma_S - \gamma_{SL} = \frac{F}{P} \tag{5}$$

where γ_{SL} is the interfacial tension between the sample plate and the liquid. If γ_L is known, we can calculate the contact angle (θ) by measuring F and P. The term, $\gamma_L \cos\theta$, is called the adhesion tension. The contact angles in the dipping-in-and-out processes are called the advancing contact angle (θ_A) and receding contact angle

(θ_R), respectively. This is performed as follows: first, the sample plate is mounted so that the bottom is 5 mm over the liquid surface; then it is lowered 20 mm at a certain constant velocity and immediately returned to its original starting point, i.e. 5 mm above the surface of the liquid.

Adhesion tension relaxation measurement

In the DCA experiments, we found that DCAs for some PVAls varied, depending on the dipping velocity. From this fact, it was hypothesized that γ_{SL} in the advancing process, and γ_S in the receding process in equation (5), exhibited a relaxation during these processes. Therefore, we measured adhesion tension relaxation using the same sample plate and instrument as for the DCA. The measurement was performed as follows: first, the sample plate was mounted so that the bottom was just in contact with the liquid surface; then it was lowered 10 mm at a velocity of 100 mm min^{-1} and stopped. At this position, the force ($F_A(t)$) applied to the sample plate in the advancing process was measured as a function of elapsed time (t) for 30 min. After that, the plate was lowered a further 10 mm, and after an interval of 30 min, it was returned to the previous position, and $F_R(t)$ in the receding process was similarly measured for 30 min. Here $F_A(t)$ and $F_R(t)$ could be described, respectively, as follows

$$F_A(t) + F_b = P\gamma_L \cos\theta_A(t) = P(\gamma_{S,A}(t) - \gamma_{SL,A}(t)) \quad (6)$$

$$F_R(t) + F_b = P\gamma_L \cos\theta_R(t) = P(\gamma_{S,R}(t) - \gamma_{SL,R}(t)) \quad (7)$$

where the buoyancy F_b was a constant value that did not depend on time.

As the surface tension of the sample plate did not depend on the elapsed time in the advancing process, $\gamma_{S,A}(t)$ become a constant value. Then equation (6) can be rewritten as

$$F_A(t) + F_b = P\gamma_L \cos\theta_A(t) = P(\gamma_S - \gamma_{SL,A}(t)) \quad (8)$$

Therefore, the variation of $F_A(t)$ with elapsed time was due only to that of $\gamma_{SL,A}(t)$, which depended on the rate of re-orientation of the polar groups to the polymer/water interface.

On the other hand, in the receding process, as the surface of the plate was hydrated in water, the interfacial tension of the sample plate to water did not depend on the elapsed time. Therefore $\gamma_{SL,R}(t)$ was rewritten to $\gamma_{SL,aq.}$, where $\gamma_{SL,aq.}$ was the interfacial tension of the hydrated copolymer/water interface.

Equation (7) can be rewritten as

$$F_R(t) + F_b = P\gamma_L \cos\theta_R(t) = P(\gamma_{S,R}(t) - \gamma_{SL,aq.}) \quad (9)$$

Therefore, the variation of $F_R(t)$ was due only to that of $\gamma_{S,R}(t)$, which depended on the rate of re-orientation of alkyl side chain in the surface of the plate which was being retracted from the water into the air.

X-ray photoelectron spectroscopy

X-ray photoelectron spectra (XPS) were measured by a Shimazu Manufacturing Ltd. ESCA 850 X-ray photoelectron spectrometer, using a MgKα X-ray source. The X-ray gun was operated at 8 kV and 30 mA, and the analyser chamber pressure was 1×10^{-6}–10^{-7} Pa. Depth profiles were determined using the variable photoelectron take-off angle method. For this experiment, two types of sample holders, whose take off angles (ϕ) were 90 and 15°, were used. The sampling depth for each take off angle $d(\phi)$ is described as follows

$$d(\phi) = d \sin\phi \quad (10)$$

where d is the sampling depth for the take-off angle $\phi = 90°$.

RESULTS

Dynamic contact angle

Figure 2 shows the dynamic contact angle for PVAls, dipping into and out of water, as a function of the number of carbon atoms in the alkyl side chain at dipping velocity = 20 mm min^{-1}. Advancing contact angle (θ_A) increased with an increase in side-chain-length and decreased after reaching the maximum value. Receding contact angle (θ_R) initially increased with side-chain-length for C2, C3 and C4, and we had low, similar, values (about 40°) from C6 to C12, and high values (about 80°) for C16 and C18.

Figure 3 shows θ_A plotted against dipping velocity (DV) for PVAls. For PVAls with side chains from C6 to C12, θ_A increased with an increase in DV and did not exhibit remarkable variation from the other PVAls. θ was determined by γ_S and γ_{SL} as shown in equation (5).

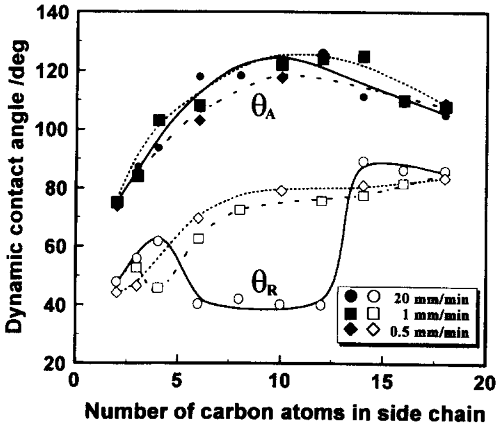

Figure 2 Dynamic contact angles for poly(vinyl alkylate)s as a function of the number of carbon atoms in side chain

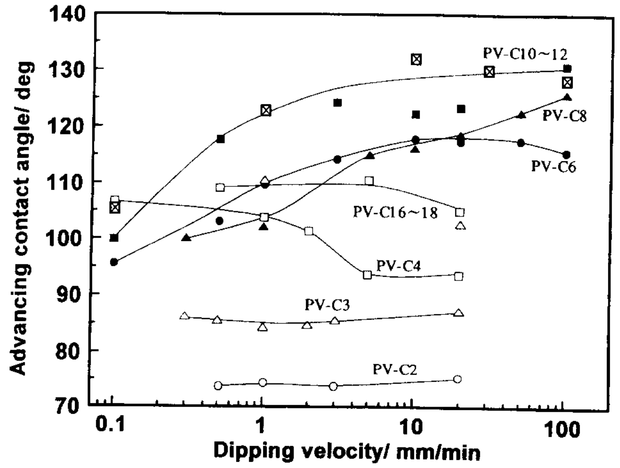

Figure 3 Relationships between advancing contact angle and dipping velocity for poly(vinyl alkylate)s having different side chain length

In the advancing process, γ_S maintained a constant value, and γ_{SL} could be varied by the re-orientation of a polar component to the water/polymer interface. The increase in θ_A from C6–C12 suggested that the re-orientation of the ester group of PVAls occurred within the time-scale measured. Conversely, θ_A did not vary with DV for C2, C3, C4, C16 and C18, since it was difficult for the re-orientation to occur because of the relatively large intermolecular interaction via the polar ester group for C2, C3 and C4, and the long alkyl side chain for C16 and C18.

Figure 4 shows θ_Rs plotted against DV for PVAls. θ_Rs showed a low value independent of DV for C2, increased with DV for C3 and C4, decreased for C6, C8, C10 and C12, and showed a high value independent of DV for C16 and C18. It was clear that reorganization of surface molecular structure did not take place in the surface of C2, C16 and C18 within the time scale measured. For the other PVAls, θ_Rs showed the complex behaviours. In the receding process, contact angle was determined by γ_S of the retracted part of the sample plate, and γ_{SL}. As both γ_S and γ_{SL} relaxed during the dipping out process, θ_Rs showed such complex behaviours. We will describe more detail on these results later.

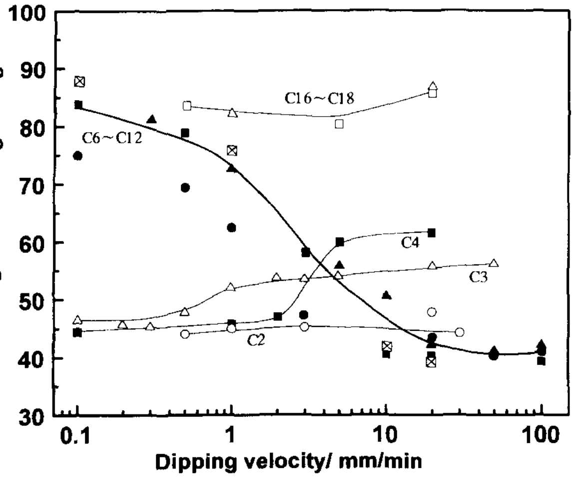

Figure 4 Relationships between receding contact angle and dipping velocity for poly(vinyl alkylate)s having different side chain length

Adhesion tension relaxation

Figure 5 shows the adhesion tension relaxation ($F_A(t)$) for PVAls as a function of the elapsed time. For C6, C8, C10 and C12, $F_A(t)$s increased with elapsed time, and did not show remarkable variation for the others, within the elapsed time shown in the figure. It was observed, however, that they increased slightly for 30 min for C3, C4, C16 and C18. This increase was due to the re-orientation of the polar group to the polymer/water interface, resulting in a reduction of $\gamma_{SL,A}(t)$ in equation (6) and (8). It was clear that the alkyl side chain for PVAls with C6–C12 have high mobility and easily re-orient to the interface.

Figure 6 shows $F_R(t)$s as a function of elapsed time. The behaviours of $F_R(t)$s for PVAls could be classified into three types. The first type had high values of $F_R(t)$s for C2, C3 and C4, and did not show relaxation. The second type had $F_R(t)$s for C6, C8, C10 and C12 that showed a large relaxation. The third type had low values of $F_R(t)$s for C14, C16, and C18, and did not show relaxation. The decrease in $F_R(t)$ was due to the re-orientation of alkyl side chain to the surface that retracted from the water to the air, resulting in a reduction of $\gamma_{S,R}(t)$ in equations (7) and (9).

X-ray photoelectron spectroscopy

The atomic ratios of oxygen (O_{1S}) to carbon (C_{1S}) for PVAls are shown in *Table 1*, via X.p.s. measurement, using two take-off angles. Atomic ratios of 90° take-off-angles show approximately the same values as those calculated from the molecular structure, while those of 15° show lower values than 90°. From these facts, it is clear that alkyl side chains, having low surface free energy, selectively adsorb to the outermost polymer surface layer.

DISCUSSION

PVAls exhibit a relatively large contact angle hysteresis ($\Delta\theta = \theta_A - \theta_R$), as shown in *Figure 2*. Factors responsible for contact angle hysteresis of a polymer include: (1) surface contamination; (2) surface roughness; (3) heterogeneity of the surface structure; (4) re-orientation or mobility of the surface segment; (5) swelling; (6) deform-

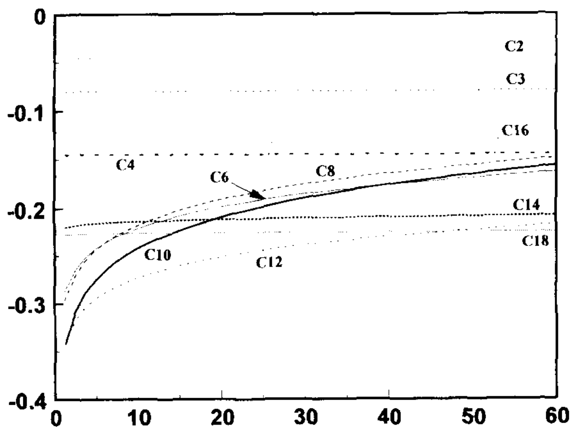

Figure 5 Adhesion tension relaxation in the advancing process for poly(vinyl alkylate)s

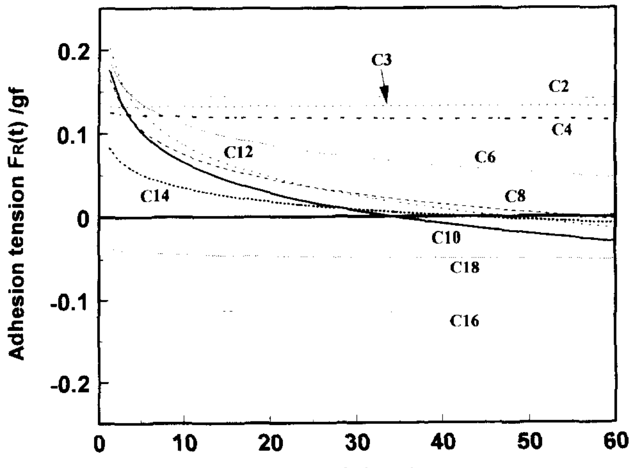

Figure 6 Adhesion tension relaxation in the receding process for poly(vinyl alkylate)s

ation, and so on. The most important factor in this study is the re-orientation or mobility of a segment of the polymer surface. On a polymer surface which has a high molecular mobility, a re-organization of surface structure takes place when the surface is moved into a different medium. PVAls of C6, C8, C10 and C12 show large $\Delta\theta$. These polymers have large θ_A, but have low θ_R, since the polar group can be re-oriented to the water/polymer interface in water, resulting in a reduction of γ_{SL} in equation (5). Conversely, it is difficult with PVAls with short (<C6) or very long (>C14) side chains for reorientation to occur, since the molecular movement is restricted by the strong intermolecular interaction of the main chain or the long alkyl side chains, respectively.

We[7] have already reported the surface tension of PVAls in relation to alkyl side chain length. For the discussion, we showed surface tension (γ) and its component due to dispersion force (γ^d) and polar force (γ^p) as a function of the number of carbon atoms in the alkyl side chain for PVAl in *Figure 7*. Surface and interfacial tension was measured via sessile bubble and sessile drop methods respectively. γ^d and γ^p were calculated via Fowkes equation using interfacial tension of PVAl in contact with polyethylene. Surface tension initially decreased with an increase in the side-chain-length, and after reaching the minimum value at C8, it increased again, γ^d increased slowly and γ^p decreased rapidly. From these results it was clear that the initial decrease in surface tension was due to decrease of the polar component, and the increase after the minimum was due to increase of the dispersion component. It was also shown that PVAls with short-side-chains had relatively strong polarity. In addition, we had observed via d.s.c. measurement that PVAls with C16 and C18 could crystallize by interaction of the alkyl side chains. Therefore these PVAls had relatively large receding contact angles resulting in small $\Delta\theta$s. We also measured θ_A, θ_R and $\Delta\theta$ for polyethylene (PE) and polypropyrene (PP), and obtained 100, 79, and 27, and 114, 82 and 22°, respectively. These values for C14, C16 and C18 were equivalent to those for PP.

It has been reported that for poly(alkyl acrylate)s, a T_g, which was responsible for intermolecular cohesion energy similar to surface tension, exhibited the same dependency of side chain length surface tension which was shown in *Figure 7* for PVAl. The advancing contact angles for PVAls increased, at first, with an increase in the chain length, and after a maximum at C10, slightly decreased as shown in *Figure 2*. This behaviour corresponded to that of the surface tension. That is, on the lower surface tension polymer, water showed the higher contact angle, showing the lower wettability.

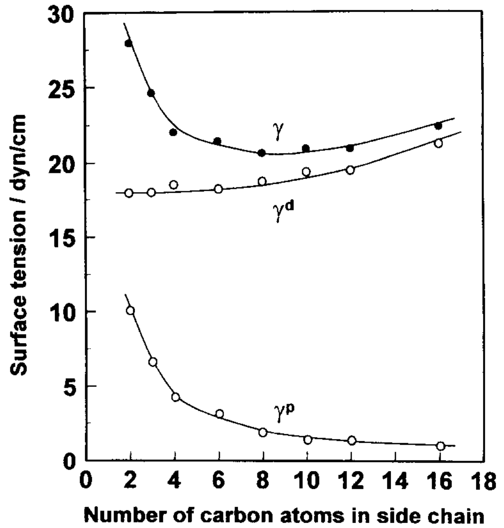

Figure 7 Dependence of surface tension (γ) and its components due to dispersion force (γ^d) and polar force (γ^p) on the number of carbon atoms in the side chain of poly(vinyl alkylate)s at 150°C

On the other hand, the receding contact angles showed a complex behaviour. For slow dipping (DV = $0.5\,\mathrm{mm\,min^{-1}}$), θ_R monotonically increased with an increase in the side chain length. For faster dipping (DV = $20\,\mathrm{mm\,min^{-1}}$), however, it initially increased with an increase in the side chain length, after reaching maximum value at C4, decreased to 40° in the region from C6 to C12, and showed large values approximately as for PE or PP for C16 and C18. Van Damme *et al.*[10] have shown approximately the same behaviour of θ_R for poly(*n*-alkylmethacrylate)s (PAMAs) as our results for PVAl. However, θ_R of PAMA had a maximum value of 75° at C6 and a minimum of 40° at C12. In contrast, our results of θ_R for PVAls had a maximum value of 60° at C4, and a minimum of 40° in the region from C6 to C12. It was clear from these facts that PVAls of C6–C12 were more mobile than PAMAs of the same alkyl side chain.

As shown in *Figure 3*, θ_A for C6, C8, C10 and C12 increased with an increase in DV. θ_A was determined by γ_S and γ_{SL} in equation (5). In the advancing process, γ_S could not vary but γ_{SL} was relaxed by reorientation of polar group. It took a few minutes for $F_A(t)$ of these polymers to equilibrate as shown in *Figure 5*. Therefore, in a faster dipping, the meniscus line of the water to the sample plate progressed so fast that there was not enough time for the polar group to re-orient to the water/polymer interface. θ_As displayed high values since the adhesion tension was determined by a low γ_S and high γ_{SL}. Conversely, in a slower dipping, since the polar group was able to re-orient, following the progress in the meniscus line, adhesion tension was determined by a low γ_S and a reduced γ_{SL}, resulting in a low θ_A. On the other hand, as shown in *Figure 4*, θ_R for C3 and C4 increased with an increase in DV and decreased for C6–C12. θ_R was determined by the γ_S of the sample plate retracted from the water into the air, and γ_{SL}. As it took a few minutes for $F_R(t)$ to equilibrate, as shown in *Figure 6*, the sample plate was retracted before equilibration in the receding process. Therefore, both γ_S and γ_{SL} varied during the receding process. For relatively unmobile polymers (C3 and C4), it took such a long time for the polar group to re-orient that the sample plate was retracted before the reduction of γ_{SL} occurred in a faster dipping process. While, in very slow dipping, even for these PVAls, as there was a little time to re-orient, θ_{RS} showed low values.

On the other hand, as the re-orientation of polar groups could easily take place for highly mobile PVAls (C6–C12), θ_Rs displayed the low values, even if in a faster dipping. In addition, in a slower dipping, as the re-orientation of alkyl chain to the surface which retracted from the water into the air could occur, to reduce γ_S, θ_Rs showed high values.

It was clear that PVAls with the side chains of C6–C12 had very large molecular mobility, as described above. In

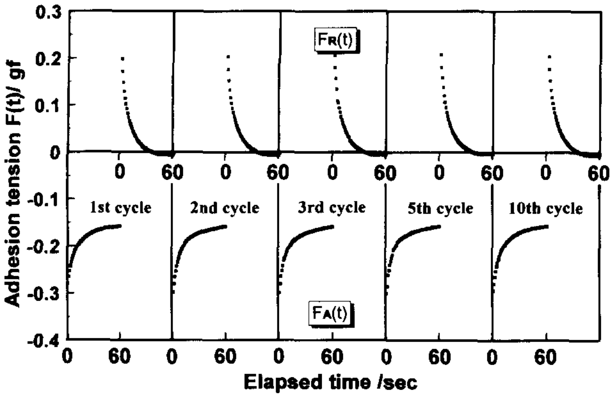

Figure 8 Reproducibility of adhesion tension relaxation for PVAl (C10)

addition, this phenomenon was able to become clearer by adhesion tension relaxation. As shown in *Figure 5*, $F_A(t)$ increased with elapsed time for C6–C12. This was due to the relaxation of $\gamma_{SL,A}(t)$ in equation (8). Takahara *et al.*[14] have also reported that adhesion tension increases with elapsed time for some segmented poly(ether urethane ureas). It took a few minutes for $F_A(t)$ to equilibrate for PVAls with side chain of C6–C12. It was clear that these PVAls had a very high mobility and these polar groups re-oriented very quickly. θ_Rs of these PVAls had approximately the same value of 40° independent of the side-chain-length, in the region of DV $> 10\,\mathrm{mm\,min^{-1}}$ as shown in *Figure 4*. $F_R(t)$s for these PVAls decreased with an increase in elapsed time. During the measurement of $F_R(t)$s, $\gamma_{SL,aq.}$, in equation (9), maintained a constant value, since the sample plate was retracted after reaching equilibrated state elapsed in water for 30 min, and $\gamma_{S,R}(t)$ decreased with elapsed time because the alkyl side chains re-oriented to the polymer surface, which dipped out from the water to the air. Therefore $F_R(t)$s decreased with elapsed time, because they were determined by the reducing $\gamma_{S,R}(t)$ and the constant $\gamma_{SL,aq.}$. It was clear that these PVAls had very large mobility, because both $F_A(t)$s and $F_R(t)$s varied quickly with elapsed time.

However, for PVAls of C2–C4 and C14–C18, both $F_A(t)$ and $F_R(t)$ exhibited only a little increase and decrease, respectively, and did not equilibrate within the time measured (30 min), even though that was not shown in the figures. It was shown that the re-orientation of the polar group to the water/polymer interface and the alkyl side chain to the surface retracted from the water to the air very slowly, because these PVAls had little mobility. It was shown that the molecular mobility drastically varied from C4 to C6, and from C12 to C14.

In order to confirm reproducibility, ATR measurements for C10 were repeated for 10 successive cycles, including both advancing and receding processes for 5 min. ATRs of the 1st, 2nd, 3rd, 5th and 10th cycle were shown in *Figure 8*. ATRs of the 10th cycle exactly reproduced the 1st.

CONCLUSION

The surface mobility of alkyl side chains of poly(vinyl alkylate)s (PVAls) were investigated via DCA, ATR and XPS measurement. These polymers exhibited large contact angle hysteresis when they were dipped into and out of water. Both advancing and receding contact angle (θ_A and θ_R) for PVAls, having side chain from C6 to C12, increased with an increase in the dipping velocity (DV) but did not exhibit remarkable variation for the other PVAls. Advancing adhesion tension ($F_A(t)$) for PVAls having side chains from C6 to C12, increased with elapsed time and receding adhesion tension decreased, but neither tension showed remarkable variation for the others. These phenomena were explained by the adsorption and re-orientation of the polar group or alkyl side chain to the interface between polymer and water or polymer surface, respectively, so as to minimize the interfacial or surface free energy. From these results we concluded that PVAls having side chains from C6 to C12 had very large surface molecular mobility, but other PVAls had little mobility.

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