pronounced for propagation than for initiation, which might be interpreted by a decrease of reactivity of the cationic species when increasing the bulkiness of the side group. A detailed comparison of our chemically initiated reactions with recent data reported about bulk and solution radiation-induced ionic polymerization of vinyl ethers leads to a good agreement (EVE apart) between the two systems and supports the existence of equilibria between free ions of different reactivities—bare, solvent solvated, and chain solvated—depending upon the nature of the side group. It seems thus that the solvation of growing cations by CH_2Cl_2 previously proposed by Stannett et al. may be considered in cationic polymerization.

Acknowledgment. We thank Dr. A. Deffieux and Professor G. Sauvet for stimulating discussions.

Registry No. MVE, 107-25-5; EVE, 109-92-2; IPVE, 926-65-8; $Ph_3C^+SbCl_6^-$, 1586-91-0.

References and Notes

(1) Subira, F.; Sauvet, G.; Vairon, J.-P.; Sigwalt, P. *J. Polym. Sci., Polym. Symp.* **1976**, *56*, 221.
(2) Bawn, C. E. H.; Fitzimmons, C.; Ledwith, A.; Penfold, J.; Sherrington, D. C.; Weightman, J. A. *Polymer* **1971**, *12*, 119.
(3) Chung, Y. J.; Rooney, J. M.; Squire, D. R.; Stannett, V. T. *Polymer* **1975**, *16*, 527.
(4) Hayashi, Ka.; Hayashi, K.; Okamura, S. *J. Polym. Sci., Polym. Chem. Ed.* **1971**, *9*, 2305.
(5) Goineau, A. M.; Kohler, J.; Stannett, V. T. *J. Macromol. Sci., Chem.* **1977**, *A11*, 99.
(6) Stannett, V. T.; Garreau, H.; Ma, C. C.; Rooney, J. M.; Squire, D. R. *J. Polym. Sci., Polym. Symp.* **1976**, *56*, 233.
(7) Ledwith, A.; Lockett, E.; Sherrington, D. C. *Polymer* **1975**, *16*, 31.
(8) Ma, C. C.; Rooney, J. M.; Squire, D. R.; Stannett, V. T. *Polymer* **1979**, *20*, 317.
(9) Subira, F.; Vairon, J.-P.; Sigwalt, P. Proceedings of the 28th IUPAC Symposium on Macromolecules, Amherst, 1982, 151.
(10) Deffieux, A.; Hsieh, W. C.; Squire, D. R.; Stannett, V. T. *Polymer* **1981**, *22*, 1575.
(11) Deffieux, A.; Hsieh, W. C.; Squire, D. R.; Stannett, V. T. *Polymer* **1982**, *23*, 65.
(12) Hsieh, W. C.; Deffieux, A.; Squire, D. R.; Stannett, V. T. *Polymer* **1982**, *23*, 427.
(13) Deffieux, A.; Young, J. A.; Hsieh, W. C.; Squire, D. R.; Stannett, V. T. *Polymer* **1983**, *24*, 573.
(14) Desai, V. R.; Suzuki, Y.; Stannett, V. *J. Macromol. Sci., Chem.* **1977**, *A11*, 133.
(15) Sauvet, G.; Moreau, M.; Sigwalt, P. *Macromol. Chem., Macromol. Symp.* **1986**, *3*, 33–46.
(16) Ledwith, A.; Woods, H. J. *J. Chem. Soc., Part B* **1966**, 753.
(17) Ledwith, A.; Woods, H. J. *J. Chem. Soc., Part B* **1970**, 310.
(18) Yuki, H.; Hatada, K.; Takeshita, M. *J. Polym. Sci., Polym. Chem. Ed.* **1969**, *7*, 667.
(19) Deffieux, A.; Stannett, V.; Wang, A.; Young, J. A.; Squire, D. R. *Polymer* **1983**, *24*, 1469.
(20) Matyjaszewski, K.; Slomkowski, S.; Penczek, S. *J. Polym. Sci., Polym. Chem. Ed.* **1979**, *17*, 2413.
(21) Brezinska, K.; Matyjaszewski, K.; Penczek, S. *Makromol. Chem.* **1978**, *179*, 2387.
(22) Ma, C. C.; Garreau, H.; Squire, D. R.; Stannett, V.; Littlejohn, M. A. *J. Macromol. Sci., Chem.* **1977**, *A11*, 1613.
(23) Plesch, P. H.; Stannett, V. T. *J. Macromol. Sci., Chem.* **1982**, *A18*, 425.
(24) Rooney, J. M. *J. Polym. Sci., Polym. Symp.* **1976**, *56*, 39.
(25) Goka, A. M.; Sherrington, D. C. *Polymer* **1975**, *16*, 819.
(26) Kunitake, T.; Takarabe, K. *Macromolecules* **1979**, *12*, 1067.
(27) Pepper, D. D. *J. Polym. Sci., Polym. Symp.* **1976**, *56*, 29.
(28) Bawn, C. E. H.; Ledwith, A. *Q. Rev., Chem. Soc.* **1962**, *16*, 361.
(29) Subira, F. Thèse de Doctorat es-Sciences, Univ. P. et M. Curie, Paris, 1981.
(30) Sawada, H. In *Thermodynamics of Polymerization*; Dekker: New York, 1976; p 85.
(31) Laidler, K. J.; Eyring, H. *Ann. N.Y. Acad. Sci.* **1940**, *39*, 103.
(32) Kamlet, M. J.; Abboud, J. L.; Taft, R. W. *J. Am. Chem. Soc.* **1977**, *99*, 6027.
(33) Gardner Swain, C.; Swain, M. S.; Powell, A. L.; Alunni, S. *J. Am. Chem. Soc.* **1983**, *105*, 502.
(34) Suzuki, Y.; Chudgar, A.; Rooney, J. M.; Stannett, V. *J. Macromol. Sci., Chem.* **1977**, *A11*, 115.

Adsorption of Sodium Dodecyl Sulfate onto α-Olefin/Maleic Acid Copolymers in Aqueous Solutions

M. J. McGlade* and J. L. Olufs

S. C. Johnson & Son, Inc.—Physical Research, Racine, Wisconsin 53403.
Received October 13, 1987

ABSTRACT: The fluorescence anisotropy of the anthryl group attached to poly(1-decene-*co*-maleic acid), PDMA, poly(1-tetradecene-*co*-maleic acid), PTMA, and poly(1-octadecene-*co*-maleic acid), POMA, has been examined at pH 8 as a function of sodium dodecyl sulfate, SDS, concentration. Adsorption of SDS onto the copolymer occurs at partial ionization of the copolymer resulting in an expansion of the copolymer coil. Expansion of the copolymer is facilitated by SDS destabilization of localized copolymer hydrophobic domains.

Introduction

Fluorescence depolarization or fluorescence anisotropy studies of covalently tagged macromolecules have proven to be an excellent way to probe the dynamics of intramolecular reorientation and of intermolecular interactions in solution.[1-3] The results provide insight into both the local environment and the nature of interactions between macromolecules and solvent systems.

In a previous study[4] we investigated the interaction between SDS and aqueous alkali-soluble α-olefin/maleic acid copolymers using extrinsic fluorescence probes. The fluorescence results gave indirect evidence for SDS interaction with the anionic polyelectrolytes. In this study we investigate the interaction between SDS and aqueous alkali-soluble α-olefin/maleic acid copolymers which are covalently labeled with 9-(hydroxymethyl)anthracene, HMA, as an intrinsic fluorescence probe. The fluorescence anisotropy of the anthryl tag is a function of the freedom of mobility of the tag and has been used to study coil–globule transitions.[5]

α-Olefin/maleic acid copolymers can be considered as polymeric amphiphiles under aqueous alkaline conditions. This leads to the possibility for the formation of polymeric micelles. The micellar structure would depend upon molecular weight, composition, sequential arrangement of repeat units, solution pH, and ionic strength. Interaction of SDS with these copolymers would, in turn, depend upon these properties.

Surfactant/polymer interactions have been studied by using other techniques also such as viscometry, surface

0024-9297/88/2221-2346$01.50/0

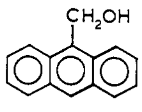
Table I
Molecular Weight Data for α-Olefin/Maleic Anhydride Copolymers

polymer	M_w	M_n	M_w/M_n
PDMA	19030	7120	2.67
PTMA	19300	6930	2.78
POMA	21420	7060	3.03

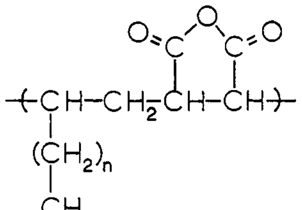
tension conductivity, electrophoretic mobility, ion-selective and surfactant-selective electrodes, small-angle neutron scattering, NMR, and dye solubilization. The majority of surfactant/polymer interaction studies involve ionic surfactants with neutral polymers[6-13] or ionic surfactants with polyelectrolytes of opposite charge.[14-16] Surfactant/polymer interactions have been reviewed.[17]

Experimental Section

Materials. Sodium dodecyl sulfate was obtained from Fluka as 99% pure and used without further purification. 9-(Hydroxymethyl)anthracene (I) was obtained from Aldrich and was recrystallized 3 times from ethanol. Poly(1-decene-*co*-maleic anhydride) (IIa), poly(1-tetradecene-*co*-maleic anhydride) (IIb), and poly(1-octadecene-*co*-maleic anhydride) (IIc) were obtained from Gulf Oil Chemical Co. The molecular weights, determined by GPC, for all copolymers used are listed in Table I.



I



II a. n=7
b. n=11
c. n=15

The anthryl fluorescence tag was covalently attached to the copolymers by reacting the HMA with the anhydride moiety of the copolymer in tetrahydrofuran (THF) at room temperature. The anhydride was converted to the sodium carboxylate salt by reaction with concentrated sodium hydroxide at 85 °C. The disodium salt of the copolymer was precipitated into methanol and washed extensively with fresh methanol.

Capillary column gas chromatographic analysis of a THF washing of the copolymer sodium salt did not show any free HMA or α-olefin free monomer. GPC results of the acid form of the high molecular weight copolymer obtained by using refractive index, RI, and fluorescence detection also did not show unreacted HMA. Superposition of the RI and fluorescence detector responses revealed a slightly broader RI response on the low molecular weight end. The degree of labeling, determined by UV absorption, is approximately one anthryl label per 390 copolymer repeat units. The concentration of HMA in a 0.5 g/L solution of the copolymer was typically on the order of 4×10^{-6} M.

All stock solutions at pH 8 were prepared with pH 8 buffer (Trizma 8.0, Sigma Chemical Co.). 9-Methylanthryl carboxylate esters have been shown to be stable to acid and base-catalyzed acyl–oxygen cleavage in oxygenated solvents.[18]

Methods. Fluorescence lifetime measurements were obtained on a SLM 4800S fluorimeter (SLM–Aminco, Urbana, IL) by using the phase-shift and demodulation method[19] with 1,4-bis[2-(4-methyl-5-phenyloxazolyl)]benzene (DMPOPOP)/ethanol as the reference, 1.45 ns.[19] The modulation frequency was 18 MHz, and the emission polarizer was set at 54.7° to eliminate polarization effects on the lifetime measurement. The lifetimes calculated from the phase shift and demodulation were averaged.

Table II
Fluorescence Lifetime and Anisotropy for HMA-Labeled PTMA at pH 8 at Various SDS Concentrations

[SDS], mol/L	τ, ns	r
0	7.19	0.169
0.002	7.04	0.160
0.010	6.87	0.152

Steady-state fluorescence polarization measurements were made by using an SLM 4800S fluorimeter configured for the simultaneous detection of the parallel and perpendicular components of the fluorescence (T-format geometry). Polarization measurements corrected for instrument response are given by

$$P = (I_V/I_H - G)/(I_V/I_H + G) \tag{1}$$

where I_V and I_H are the fluorescence intensities in the vertical and horizontal directions, respectively, using vertically polarized incident light. G is the correction factor for instrument response obtained by using horizontally polarized incident light.[19] Polarization is converted to anisotropy by

$$r = 2P/(3 - P) \tag{2}$$

Excitation of the anthryl tag was at 366 nm, and the polarized emission was measured at 435.8 nm by using interference filters. The temperature for all measurements was 20 °C.

Results and Discussion

The copolymers used in this study are aqueous alkali soluble and have been shown by dye solubilization[4] and fluorescence quenching[20] to form micellar-like aggregates. Dubin and Strauss,[21] using intrinsic viscosity measurements, obtained results for ethyl and butyl vinyl ether maleic acid copolymers, at various degrees of ionization, which showed that urea, a denaturant, expanded the molecular dimensions of the copolymer in both the hypercoiled and extended conformation. Urea appeared to destabilize the hypercoiled state by enhancing the solvent affinities of the hydrophobic side chain as well as the polar backbone of the polyacid. Anufrieva et al.,[22] investigating models of globular protein denaturation by using poly(methacrylic acid) (PMA), found that aliphatic alcohols destroyed the local compact structure of PMA better if the alcohol possessed more hydrophobic groups. Furthermore, from intrinsic viscosity studies of PMA in water–methanol mixtures, it was shown that alcohol leads not only to the destabilization of the local compact structures but also to the unfolding of the macromolecule as a whole.

The conformation of the α-olefin/maleic acid copolymer in solution will be determined by the mutual interactions of the nonpolar paraffinic pendant side chains and hydrocarbon backbone with the polar ionic carboxylate groups as well as the interactions between the copolymer segments and the aqueous phase. For a given copolymer solution conformation, a number of intramolecular interfaces would exist between the polar and nonpolar segments.[23] On a molecular level, an interface would exist between the nonpolar segments of the copolymer and the polar aqueous phase. It is at these interfaces that nonspecific hydrophobic adsorption of the surfactant has been shown to occur.

The average fluorescence lifetime and anisotropy values for HMA-labeled PTMA at three SDS concentrations are given in Table II. The average fluorescence lifetime and anisotropy decrease with increasing SDS concentration. The fluorescence lifetime of the anthryl tag was measured with the emission polarizer set at the "magic angle" of 54.7°, and therefore changes in the lifetime values reflect only changes in the polarity of the environment and not viscosity effects. The fluorescence lifetime of anthracene derivatives is known to be sensitive to solvent polarity.

To gain a clearer understanding of the effect of the SDS-PTMA interaction on the anthryl tag, we consider the relationship between τ and r. For small molecules in dilute solution the relationship is given by the Perrin equation as

$$r_0/r = 1 + \tau/\phi \qquad (3)$$

where r_0 is the limiting fluorescence anisotropy in the absence of motion of the probe and ϕ is the rotational correlation time. From the Stokes–Einstein equation for a spherical molecule in an isotropic medium of smaller solvent molecules

$$\phi = \eta V/RT \qquad (4)$$

where η is the viscosity of the medium, V the hydrodynamic rotational volume, R the gas constant, and T the absolute temperature. Substituting 4 into eq 3, we obtain

$$r_0/r = 1 + (RT/\eta V)\tau \qquad (5)$$

Fluorescently labeled macromolecules usually do not satisfy the criteria of the Stokes–Einstein equation, which would permit direct calculation of the microviscosity of the probe environment from a knowledge of r_0, r, V, and τ. Nevertheless it is qualitatively useful to observe, in this case, the trend in η with decreasing τ and r. As SDS concentration increases, the resulting effect of the surfactant on the environment probed by the anthryl tag is a reduction in the local viscosity. The reduction in the local viscosity may be the result of SDS adsorption destabilizing local compact structures which in turn may lead to an expansion in the copolymer coil dimensions.

The dependence of r on SDS concentration for three copolymers of approximately equal molecular weight with varying pendant hydrophobe length is shown in Figure 1. The transitory nature of the curves indicates the presence of a distinct copolymer coil transition as SDS is added to the system. The degree of neutralization is approximately 60%, 63%, and 50% for PDMA, PTMA, and POMA, respectively. The transition point increases in the order POMA, PDMA, and PTMA with increasing SDS concentration. The order of the transition points appears to correlate with the degree of neutralization. The SDS-to-r.u. concentration ratio for the low SDS concentration transition is 0.6, 0.8, and 0.6 for PDMA, PTMA, and POMA, respectively.

All three copolymers show the same trend in r with increasing SDS concentration. The most significant difference between the three copolymers is the length of the pendant hydrophobe. This difference is predominantly reflected in the initial r values and can be related to the effect of the pendant on the conformational state of the copolymer. On the basis of a consideration of the relative insolubilities of the C_8, C_{12}, and C_{16} pendant hydrophobes in the aqueous phase, it is apparent that the longer the pendant side chain is the more collapsed the copolymer coil will be. Analogous behavior has been observed in the case of coil conformational transition for shorter chain ($<C_8$) alkyl vinyl ether as comonomers with maleic acid.[24] In the latter, conformation transitions appears at a lower degree of ionization for shorter chain length hydrophobes than for longer.

The copolymer coil conformational transition point resulting from the adsorption of SDS will depend on a number of parameters, which include the copolymer molecular weight, polydispersity in molecular weights (M_w/M_n), degree of aggregation, degree of neutralization, length of pendant hydrophobe, and comonomer ratio. Considering the number of parameters, the transition point for coil expansion is approximately the same for all three copolymers. Thus, it would appear that the contribution of the C_{16} pendant to the transition point is not significantly different from that of C_{12} or C_8. However, its effect on the slope of the transition is quite significant, as seen in the figure.

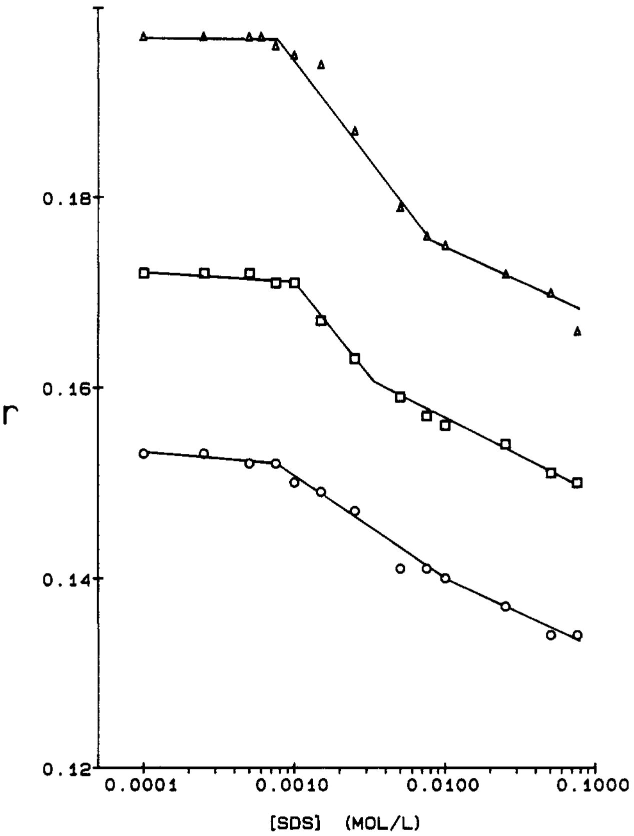


Figure 1. HMA fluorescence anisotropy of HMA-labeled PDMA (○), PTMA (□), and POMA (△) in pH 8 buffer as a function of SDS concentration. The concentration of the copolymers in repeat units is 1.2×10^{-3} mol/L.

The magnitude in the decrease in r over the SDS concentration range studied may be correlated with the degree of expansion of the copolymer coil. The change in r for SDS concentration from 0 to 0.075 M for the three copolymers shown in Figure 1 increases in the order PDMA, PTMA, POMA. The degree of expansion of the copolymer coil may be a function of the initial conformation of the copolymer prior to the addition of SDS. If the copolymer initially existed in a loosely coiled conformation, then the amount of further coil expansion facilitated by the adsorption of SDS would be expected to be less than that for a copolymer initially existing in a more compact conformation. Since the shorter pendant chain length copolymers are less coiled in the absence of SDS (and hence a correspondingly lower r value), these undergo a smaller change in r upon addition of surfactant.

Conclusion

Fluorescence anisotropy of a covalently bound anthryl tag has been used to study adsorption of SDS onto α-olefin/maleic acid copolymers as a function of copolymer pendant side-chain length. The results clearly indicate that SDS binds to the copolymer at partial ionization of the copolymer and that the result of SDS adsorption is a change in the conformational state of the copolymer. The binding of SDS may proceed gradually as coil expansion exposes more hydrophobic sites. A correlation appears to exist between the fluorescence anisotropy and pendant side-chain length for copolymers of approximately equal molecular weight.

Acknowledgment. We express our gratitude to Dr. C. Weiss and J. Hazlett for the GPC measurements and to J. Ryback for the GC analysis.

Registry No. IIa (9-anthrylmethyl ester sodium salt), 114956-82-0; IIb (9-anthrylmethyl ester sodium salt), 114956-84-2; IIc (9-anthrylmethyl ester sodium salt), 114956-83-1; sodium dodecyl sulfate, 151-21-3.

References and Notes

(1) Anufrieva, E. V.; Gotlib, Yu. Ya. *Adv. Polym. Sci.* **1981**, *40*, 1.
(2) Monnerie, L. In *Polymer Photophysics*; Phillips, D., Ed.; Chapman and Hall: New York, 1985.
(3) Blatt, E.; Jovin, T. M. In *Photophysical and Photochemical Tools in Polymer Science: Conformation, Dynamics, Morphology*; Nato ASI Series C; Winnik, M. A., Ed.; D. Reidel: Holland, 1986; p 182, 351.
(4) McGlade, M. J.; Randall, F. J.; Tcheurekdjian, N. *Macromolecules* **1987**, *20*, 1782.
(5) Ushiki, H.; Tanaka, F. *Eur. Polym. J.* **1985**, *21*, 701.
(6) Arai, H.; Horin, S. *J. Colloid Interface Sci.* **1969**, *30*, 372.
(7) Turro, N. J.; Baretz, B. H.; Kuo, P.-L. *Macromolecules* **1984**, *17*, 1321.
(8) Jones, M. N. *J. Colloid Interface Sci.* **1967**, *23*, 36.
(9) Zana, R.; Lianos, P.; Lang, J. *J. Phys. Chem.* **1985**, *89*, 41.
(10) Peiffer, D. G.; Lundberg, R. D. *J. Polym. Sci., Polym. Phys. Ed.* **1984**, *22*, 2051.
(11) Kresheck, G. C.; Hargraves, W. A. *J. Colloid Interface Sci.* **1981**, *83*, 1.
(12) Shirahama, K.; Tohodo, M.; Murahashi, M. *J. Colloid Interface Sci.* **1982**, *86*, 282.
(13) Arai, H.; Murata, M.; Shinoda, K. *J. Colloid Interface Sci.* **1971**, *37*, 223.
(14) Dubin, P.; Oteri, R. *J. Colloid Interface Sci.* **1983**, *95*, 453.
(15) Hayakawa, K.; Santerre, J. P.; Kwak, J. C. T. *Macromolecules* **1983**, *16*, 1642.
(16) Ananthapadman, K. P.; Leung, P. S.; Goddard, E. D. *Colloids Surf.* **1983**, *13*, 63.
(17) Robb, I. D. In *Anionic Surfactants, Physical Chemistry of Surfactant Action*; Surf. Sci. Ser. 11; Lucassen-Reynders, E. H., Ed.; Marcel Dekker: New York, 1981; Chapter 3.
(18) Kornblum, N.; Scott, A. *J. Am. Chem. Soc.* **1974**, *96*, 590.
(19) Lakowicz, J. R. *Principles of Fluorescence Spectroscopy*; Plenum: New York, 1983.
(20) Chu, D.-Y.; Thomas, J. K. *Macromolecules* **1987**, *20*, 2133.
(21) Dubin, P.; Strauss, U. P. *J. Phys. Chem.* **1973**, *77*, 1427.
(22) Anufrieva, E. V.; Birshtein, M. T.; Nekrasova, T. N.; Ptitsyn, O. B.; Shevelera, T. V. *J. Polymn. Sci., Part C* **1968**, *16*, 3519.
(23) Nagarajan, R.; Harold, M. P. In *Solution Behavior of Surfactants*; Mittal, K. L., Fendler, E. J., Eds.; Plenum: New York, 1982; Vol. 2.
(24) Dubin, P.; Strauss, U. P. *J. Phys. Chem.* **1970**, *74*, 2842.

Interactions between Adsorbed Polystyrene Layers in Toluene–Heptane Mixtures. Effect of Solvent Quality

Johan Marra* and Michael L. Hair

Xerox Research Centre of Canada, 2660 Speakman Drive, Mississauga, Ontario L5K 2L1, Canada. *Received July 27, 1987*

ABSTRACT: A report is given of the direct measurement of forces between mica surfaces on which PS homopolymer (M_w = 300 000) has been adsorbed from heptane–toluene mixtures. By changing the mixing ratio, polymer adsorption and the accompanying force vs distance profiles could be measured as a function of a broad range of effective solvent qualities. With PS on the surfaces, the forces at long range were always attractive independent of the solvent quality. The results point out that the forces at large surface separations are dominated by purely polymeric interactions originating from the dilute periphery of the adsorbed layers. These probably involve polymer bridging. For the bare mica surfaces there is clear evidence that below a surface separation of 5 nm, the surface-induced attraction becomes anomalously strong, leading to a stronger adhesion than expected from Lifshitz theory. A similar phenomenon may exist between polymer-bearing surfaces. As a consequence the force of adhesion becomes a function of the amount of adsorbed polymer, the solvent quality, and the surface separation at which the minimum in the force law is located. These three factors are not independent of each other, and the adhesion can be partly or totally the result of either the van der Waals attraction or the polymer bridging or the negative free energy of mixing between the interacting polymer layers. It is proposed that the sometimes observed hysteresis in the force vs distance profiles can be explained through the kinetics of the formation of polymer bridges. Although a quantitative comparison of the results with existing theories may be complicated because of the expected preferential uptake of the better solvent toluene in the adsorbed layers, the observed features are the first to illustrate the delicate interplay between mica-induced forces and polymer-induced forces.

Introduction

The technological importance of polymeric stabilization in colloidal dispersions has created a strong experimental[1-11] and theoretical[12-15] interest in the basic principles governing polymer adsorption on and polymeric interactions between interfaces. It is well-known that polymer adsorption profoundly modifies interparticle interactions.[16,17] An important application of this fact is encountered in nonpolar solvents. Due to the virtual absence of electrostatic interactions in those solvents, the adsorption or grafting of a polymer onto the surface of the particles is the only effective way to establish dispersion stability and prevent flocculation caused by the attractive van der Waals forces.

On the other hand, in paint, food, and ink technology there are applications for dispersions that are "weakly" flocculated. In these cases, the presence of an attractive interparticle interaction leads to weak particle associations that can easily be disrupted. Although such systems are usually the outcome of a complicated chemical engineering recipe, they can often be at least partly understood as dispersions in which the particles are stabilized by adsorbed or grafted polymer and suspended in a medium of moderately poor thermodynamic quality toward the stabilizing polymer. Attractive interactions between the polymers will always exist when the solvent is a worse than Θ solvent for that particular polymer. Napper[18] has formulated the general rule that the onset of dispersion