Studies of cyclic and linear poly(dimethylsiloxanes): 30. Adsorption studies on silica in solution

A. Patel
Department of Chemistry, University of York, Heslington, York YO1 5DD, UK and School of Chemistry, University of Bristol, Cantocks Close, Bristol BS8 1TS, UK

T. Cosgrove
School of Chemistry, University of Bristol, Cantocks Close, Bristol, BS8 1TS, UK

and J. A. Semlyen*
Department of Chemistry, University of York, Heslington, York YO1 5DD, UK
(Received 21 May 1990; accepted 3 July 1990)

The adsorbed amounts of cyclic and linear poly(dimethylsiloxane) fractions of heterogeneity indices $M_w/M_n \approx 1.05$ on silica were investigated by Fourier-transform infra-red spectroscopy. It has been found that at low molar masses the adsorption of cyclic polymer is greater than that of the corresponding linear polymer, but at high molar masses the reverse behaviour is found. This is in agreement with the theoretical predictions of van Lent, Scheutjens and Cosgrove. Adsorption of the polymers was investigated in two different solvents, and it was found that the adsorption was greater from hexane than from tetrachloromethane for both linear and cyclic polymers.

(Keywords: cyclic; linear; poly(dimethylsiloxanes); adsorption; silica; Fourier-transform infra-red spectroscopy)

INTRODUCTION

Polymer adsorption has been studied extensively by a wide range of experimental techniques[1]. For homopolymers it is now generally accepted that the adsorption of high-molar-mass polymers leads to a highly extended adsorbed layer[2]. The hydrodynamic thickness of this layer in the plateau of the adsorption isotherm is thought to be due to the preferential formation of tails. Both theoretical and experimental results support this view[3]. However, an unambiguous test of this proposition would be to compare adsorption results for systems in which the formation of tails was excluded. An ideal system in this respect would be to compare linear and cyclic molecules of virtually the same chemical structure, and to this end samples of poly(dimethylsiloxane) (PDMS) have been used in this study.

The preparation and properties of sharp fractions of both cyclic and linear PDMS have been described in previous papers in this series[4]. Cyclic polymers with number-average degrees of polymerization up to 500 have been obtained in gram quantities by preparative gel permeation chromatography (g.p.c.). These materials have been characterized by dilute solution[5] and bulk viscometry[6], small-angle neutron scattering[7], photon correlation spectroscopy[8], diffusion measurements[9–13] and ^{29}Si nuclear magnetic resonance (n.m.r.) spectroscopy[14].

This paper presents adsorption data for a series of cyclic and linear PDMS fractions on silica using hexane and tetrachloromethane as solvents. The results of these studies are compared with the self-consistent mean-field calculations based on the Scheutjens–Fleer (SF) theory[2,15].

EXPERIMENTAL

Materials

Fractions of linear poly(dimethylsiloxanes), $(CH_3)_3 \cdot SiO[(CH_3)_2SiO]_ySiO(CH_3)_3$, and cyclic poly(dimethylsiloxanes), $[(CH_3)_2SiO]_x$, were obtained by methods described previously[16,17].

The linear fractions, which were trimethyl-terminated, were obtained by preparative g.p.c. (polymers L1–L5), starting from Dow Corning dimethicones. The cyclic fractions were recovered from ring-chain equilibrates in toluene at 110°C before being separated into fractions by preparative g.p.c. (polymers R1–R4). Number-average molar masses M_n, number of skeletal bonds n and ratios of M_w/M_n are listed in *Table 1*.

Adsorption studies by infra-red spectroscopy

The substrate used was Aerosil A-130 fumed silica, diameter 16 nm, obtained from Degussa, which was used without treatment. The solvents were spectrophotometric-grade tetrachloromethane and h.p.l.c.-grade hexane. All adsorption measurements were carried out on a Perkin–Elmer 1720 Fourier-transform infra-red (*FT*i.r.) spectrometer.

A range of polymer solutions of known concentrations were prepared in the solvents hexane and tetrachloromethane. Each polymer solution was added directly to the substrate as received. The samples were sealed and

---

* To whom correspondence should be addressed

0032–3861/91/071313–05

Table 1 Characterization of the linear and cyclic PDMS

Fraction	n	M_n (g mol^{-1})	M_w/M_n	R_g (nm)^a
Linear PDMS				
L1	14	680	1.03	0.47
L2	134	5120	1.05	1.88
L3	350	13 110	1.05	3.03
L4	573	21 360	1.07	3.80
L5	1076	50 000	1.16	5.20
Cyclic PDMS				
R1	14	520	1.02	0.39
R2	137	5070	1.03	1.80
R3	334	12 360	1.01	2.12
R4	582	21 530	1.09	2.83

$^a R_g$ denotes the radius of gyration

thorough mixing was ensured by shaking for 48 h. The samples were then centrifuged for 20 min at 4000g and the supernatant liquid removed carefully and analysed by i.r. spectroscopy. All measurements were carried out in an i.r. solution cell (sodium chloride), with a 0.2 mm spacer for 10 scans. Calibration graphs for the peak at 1260 cm^{-1} were determined for a series of polymer solutions at different molar masses, which gave a linear dependence on concentration. From these plots the equilibrium concentration of the polymer in the supernatant solution was determined. From this difference in concentration the adsorbed amounts Γ were calculated. Adsorption isotherms were obtained as a function of molar mass. Because of the uncertainty of the absolute surface area obtained when redispersing silica in the two solvents, the adsorbed amounts Γ are expressed in milligrams per gram. The results, however, were reproducible, showing that aggregation (though of an indeterminate extent) could be effectively controlled using a standard dispersal procedure. All measurements were carried out at room temperature, 298 K.

RESULTS AND DISCUSSION

Adsorption from tetrachloromethane

Figures 1 and *2* show adsorption isotherms for both high- and low-molar-mass polymers from tetrachloromethane. It can be seen that for both samples the adsorbed amount for cyclic PDMS is greater than for the linear polymers and that the adsorption isotherms are of the low-affinity type. Neither adsorption isotherms show a clear plateau level and the adsorbed amount continues to increase slowly with concentration, which is in agreement with the results obtained by Brebner[18]. The adsorbed amount per unit surface area can be calculated assuming that the geometric area of the particle is preserved after adsorption. This approximation would give an upper bound for the surface area per molecule Γ, and these are shown in *Table 2*. The values are rather small compared to other systems[3], even for the high-molar-mass sample. The reason for this is partly due to the fact that tetrachloromethane itself has a high affinity for silica. It is proposed that the tetrachloromethane is weakly bonded to the surface hydroxyl groups of the silica by van der Waals forces. Therefore the PDMS is in competition for those sites and it is proposed that PDMS adsorbs onto the silica from tetrachloromethane by mechanism I, in *Figure 3*.

There are several mechanisms which the polymer, PDMS, is thought to adsorb on the surface of silica[19] and these are shown schematically in *Figure 3*.

One molecule of tetrachloromethane can be said to occupy approximately 0.4 nm^2 of the silica surface. The competition for surface sites by tetrachloromethane leads to the observed situation in which less polymer is adsorbed, but a greater dependence on molar mass might be expected because the polymer is attached to the surface at fewer anchor points.

Table 2 shows values of the plateau level adsorption for a series of linear and cyclic PDMS samples adsorbed from tetrachloromethane. From the adsorbed amount it is straightforward to calculate the surface area per molecule (SA/mol) and these values are also given. Although it is a rather simplistic approach, it is however instructive to compare SA/mol with the equivalent cross section of the polymer in solution. This latter value ($4\pi R_g^2$, where R_g is the radius of gyration) can be calculated for known values of R_g.

For low-molar-mass cyclics the ratio of $SA/4\pi R_g^2 > 1$ (*Table 2*) whereas at high molar masses the reverse is true. A similar behaviour is found with the linear chains, except that much smaller absolute values are found. Small chains do not form extensive tails and cyclic polymers have no tails; therefore the values of the ratio for both cyclic and linear polymers for the lowest molar mass samples are similar (*Table 2*). However, the difference begins to diverge with increasing chain length, and compared to their size in solution the cyclic molecules

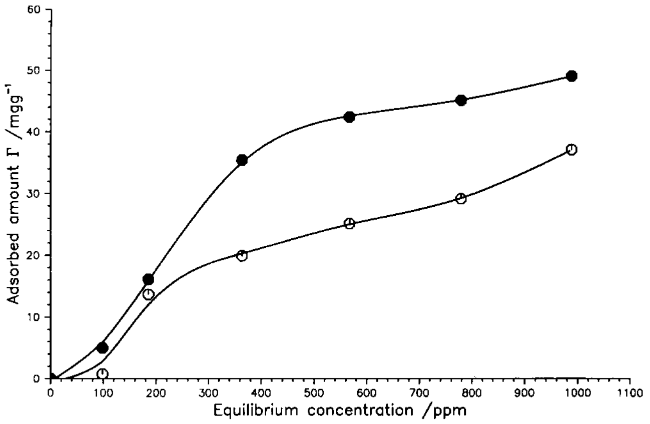

Figure 1 Adsorption isotherm of cyclic (●) $n = 14$ and linear (○) $n = 14$ PDMS adsorbed on silica from tetrachloromethane

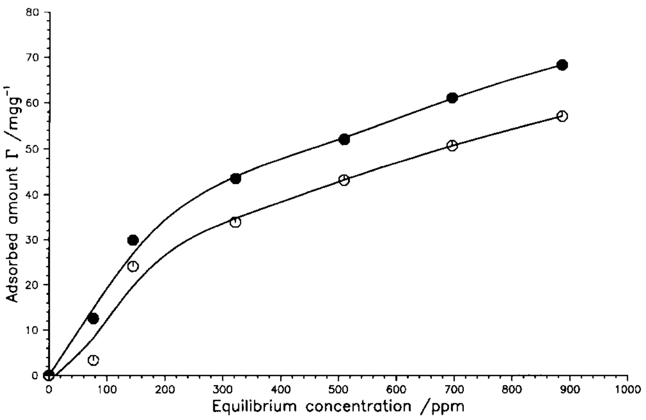

Figure 2 Adsorption isotherm of cyclic (●) $n = 582$ and linear (○) $n = 573$ PDMS adsorbed on silica from tetrachloromethane

Table 2 Results of adsorption studies

Fraction	Γ (mg m^{-2})	M_w (g mol^{-1})	No. of polymer molecules adsorbed (10^{17})	SA/mol^a (nm^2)	X-sect.^{b} (nm^2)	$SA/4\pi R_g^{2\,c}$
Cyclic PDMS in CCl_4						
R1	0.4	530	4.54	2.2	1.9	1.16
R2	0.423	5 220	0.49	20.5	22.6	0.91
R3	0.469	12 520	0.26	44.3	56.5	0.78
R4	0.546	23 440	0.14	71.3	100.6	0.71
Linear PDMS in CCl_4						
L1	0.315	690	2.75	3.6	2.8	1.29
L2	0.346	5 390	0.39	25.9	44.6	0.58
L3	0.415	13 760	0.18	55.1	115.8	0.48
L4	0.477	22 900	0.13	79.8	181.9	0.43
L5	0.623	58 000	0.06	154.7	339.3	0.46
Cyclic PDMS in hexane						
R1	0.877	530	9.96	1.0	1.9	0.53
R2	0.915	5 220	1.06	9.5	22.6	0.42
R3	1.008	12 520	0.49	20.6	56.5	0.36
R4	1.108	23 440	0.28	35.0	100.7	0.35
Linear PDMS in hexane						
L1	0.785	690	6.81	1.5	2.8	0.53
L2	0.846	5 390	0.94	10.6	44.6	0.28
L3	0.962	13 760	0.42	23.8	115.8	0.21
L4	1.138	22 900	0.30	33.4	181.9	0.18
L5	1.446	58 000	0.15	66.6	339.3	0.19

[a] Denotes the surface area per molecule adsorbed
[b] Denotes the equivalent cross-sectional area of polymer in solution ($4\pi R_g^2$)
[c] Denotes the ratio of the previous two quantities

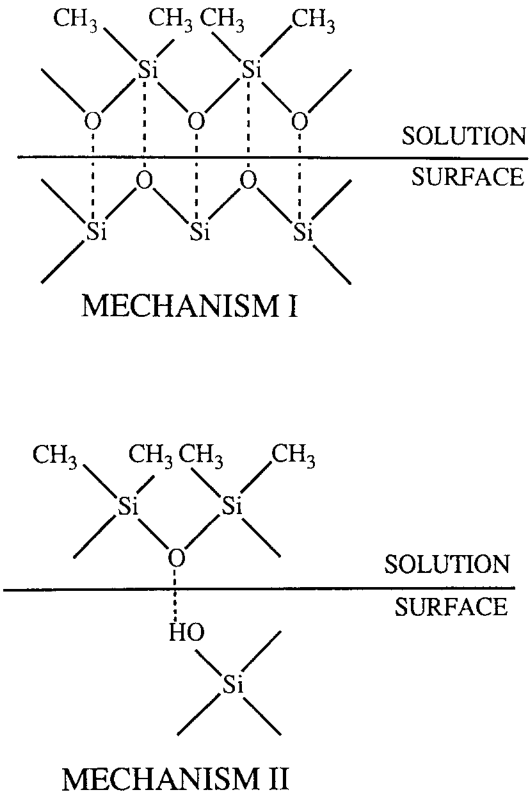

Figure 3 Some possible mechanisms of adsorption of PDMS onto the surface of silica

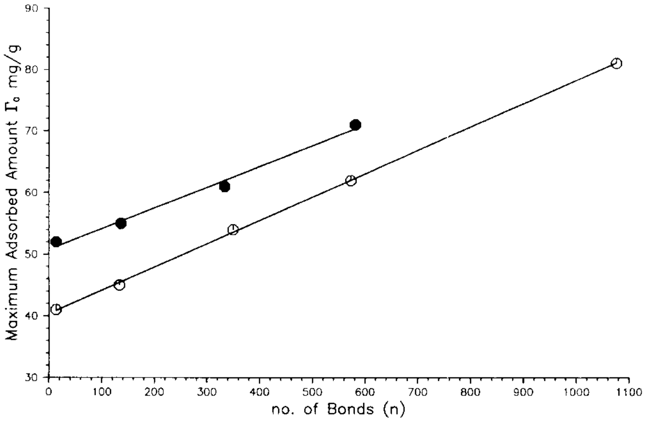

Figure 4 Plot of maximum adsorbed amount Γ_0 as a function of number of bonds n for cyclic (●) and linear (○) PDMS adsorbed on silica from tetrachloromethane

are more compact than the linear analogues. However, these calculations do not highlight all the trends that are in the data.

In *Figure 4* the adsorbed amount at 1000 ppm is plotted as a function of molar mass for both species. All of the Γ_{max} values of the cyclics are above the linear PDMS; however, the rate of increase of Γ_{max} with M_w is greater for the linear chains. Interestingly, these plots are virtually linear and suggest that at much higher values of M_w there will be a cross-over where the formation of larger tails will lead to higher Γ_{max} values for the linear

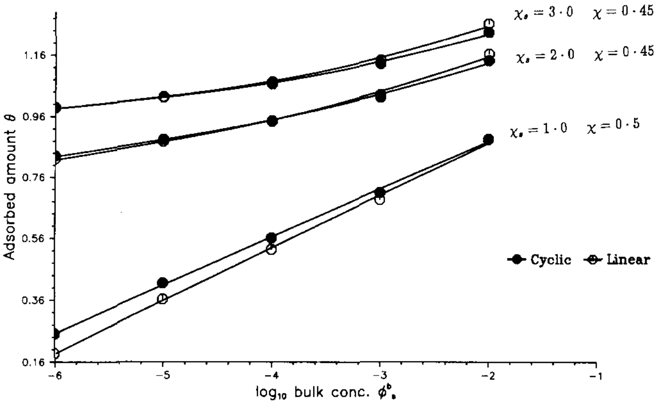

Figure 5 Plot of theoretical adsorbed amount θ as a function of the bulk concentration ϕ_s^b for cyclic (●) and linear (○) chains for $\chi_s = 1$, 2 and 3. Chain length $r = 18$

species. The cyclic polymer is more compact (compare R_g values in *Table 1*) and this leads to a higher Γ_{max}, at least at lower molar masses. In the adsorption from tetrachloromethane, the low-affinity isotherms, and the relatively low Γ_{max} values, do not strongly emphasize the difference between linear chains and rings.

Figure 5 is a theoretical plot of adsorbed amount θ against log bulk solution concentration ϕ_s^b, calculated from the SF model. Values of $\chi(0.5)$ and $\chi_s(1.0)$ have been chosen to reflect best the adsorption and solution properties of the system. One monomer has been taken to be equal to one theoretical segment. The results obtained experimentally in *Figure 4* fit well in a qualitative sense with the theoretical plot, although the absorbed difference between cyclic and linear is considerably less pronounced. *Figure 5* shows that for these thermodynamic values the adsorbed amounts for the linear polymers are increasing more rapidly than the amounts for the cyclics, and that a cross-over of the two isotherms would occur at a higher value of bulk concentration, which is in agreement with the experimental data in *Figure 4*. As the χ_s value is increased ($\chi_s = 2.0$) a cross-over is indeed seen, and for $\chi_s = 3.0$ a complete reversal is observed, whereby the linear polymer adsorbs more than the corresponding cyclic one over the whole concentration range.

Adsorption from hexane

In general, adsorbed amounts are lower from good solvents than from poor solvents due to the favourable polymer–solvent interactions that occur. However, two factors must be considered: the polymer–solvent interaction parameter χ and the segmental adsorption energy parameter χ_s. Both a high χ (poor solvent) and a higher χ_s (stronger attachments of segments) lead to higher adsorbed amounts.

Work carried out by Brebner and coworkers[18] has shown that tetrachloromethane is a poorer solvent than hexane for PDMS. The χ value measured for hexane was 0.45 and for tetrachloromethane χ was 0.5. This suggests that adsorption should be greater from tetrachloromethane than hexane. However, this was not observed, since tetrachloromethane is preferentially adsorbed on the surface of silica compared to hexane.

In *Figures 6* and *7* adsorption isotherms for both low- and high-molar-mass polymers from hexane are shown. Clearly, in comparison with *Figures 1* and *2*, the adsorption from hexane is much greater than from tetrachloromethane. This can be rationalized in that tetrachloromethane is adsorbed more strongly onto silica than hexane, hence χ_s(hexane) > $\chi_s(CCl_4)$ and χ_s is more important than χ in determining the adsorbed amount. The weak interaction of hexane with silica leaves vacant hydroxyl groups to interact with the polymer, which may then adsorb via mechanism II (*Figure 3*).

Figure 6 shows that at low molar mass the cyclic polymers adsorb to a greater extent than the corresponding linear ones, and that all the linear points are below the cyclic points. The adsorption isotherm is also of low affinity, and at low equilibrium concentration the adsorbed amounts of cyclic and linear polymers are very close. However, as the equilibrium concentration is increased, the difference in adsorbed amount (Γ) between the two increases on approaching the plateau.

Figure 7 shows that, at high molar mass, the adsorption isotherm has a higher-affinity nature at low equilibrium concentration, but even then the isotherm does not reach a definitive plateau. The absolute values of Γ in this case are much higher than for the isotherms obtained from tetrachloromethane. The difference in adsorbed amount between the cyclic and the corresponding linear polymer is less, but the reverse behaviour is observed; the linear polymer now adsorbs to a greater extent than the cyclic (all the linear points are above the cyclic points).

Comparison of the $SA/4\pi R_g^2$ values (*Table 2*) for hexane show the same trend as for CCl_4, but all values are substantially less; from hexane both linear chains and rings appear highly distorted compared to the solution

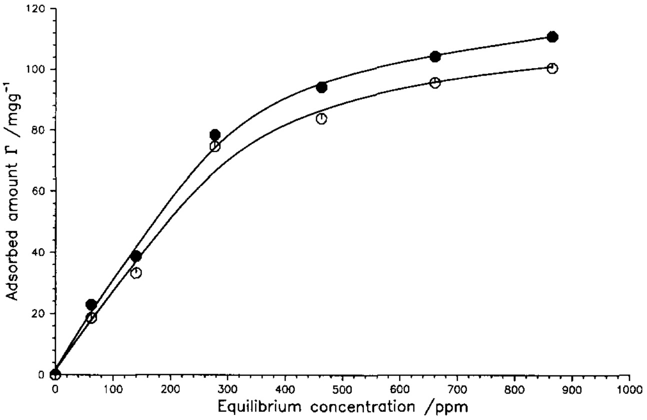

Figure 6 Adsorption isotherm of cyclic (●) $n = 14$ and linear (○) $n = 14$ PDMS adsorbed on silica from hexane

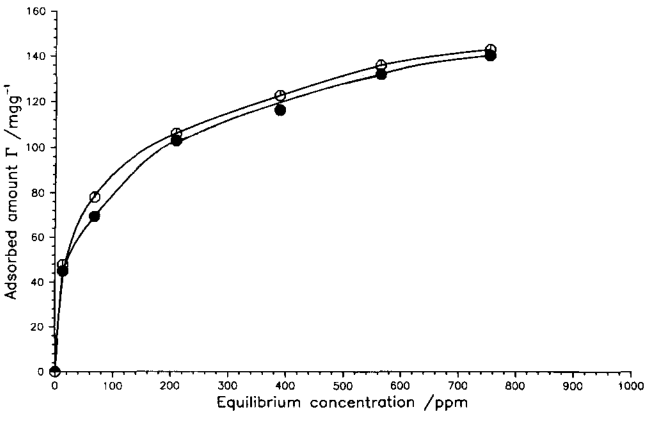

Figure 7 Adsorption isotherm of cyclic (●) $n = 582$ and linear (○) $n = 573$ PDMS adsorbed on silica from hexane

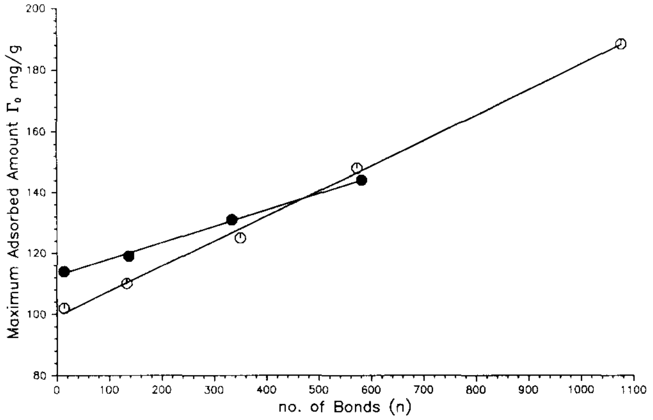

Figure 8 Plot of maximum adsorbed amount Γ_0 as a function of number of bonds n for cyclic (●) and linear (○) PDMS adsorbed on silica from hexane

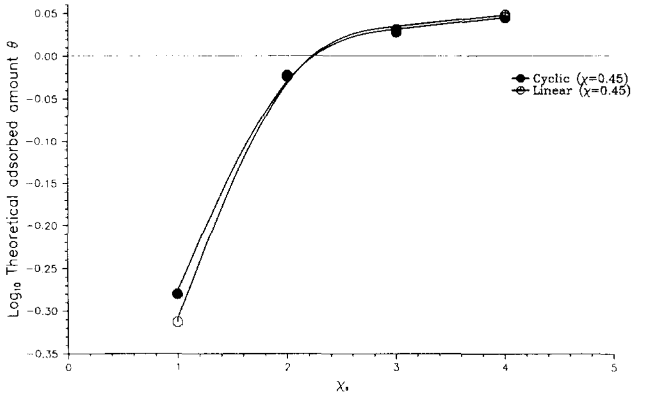

Figure 9 Plot of $\log_{10}$ theoretical adsorbed amount θ as a function of χ_s for cyclic (●) and linear (○) PDMS for $\chi = 0.45$. Chain length $r = 18$ at bulk concentration $\phi_s^b = 10^{-4}$

conformation, and hence the difference between linear and ring polymers should be more pronounced.

Figure 8 is a plot of maximum adsorbed amount against number of bonds (n) in hexane, which clearly shows a cross-over point between linear and cyclic at $n = 470$ bonds. The adsorbed amount as a function of the number of bonds is linear. These results are also in agreement with the theoretical predictions in *Figure 5*. From *Figure 5*, it can also be seen that a cross-over occurs at a lower ϕ_s^b for a higher χ_s.

In *Figure 9* a plot of the $\log_{10}$ theoretical adsorbed amount θ against χ_s is shown, with a cross-over around $\chi_s = 2.0$ for $\chi = 0.45$. If the slopes in *Figure 4* were extrapolated then a cross-over would occur at a similar value of Γ to that in *Figure 8*. It was from this theoretical plot that the χ_s values were chosen best suited to the polymer– solvent systems: $\chi_s = 2.0$ for hexane and $\chi_s = 1.0$ for tetrachloromethane. With reference to *Figure 5* it can be seen clearly that χ_s plays an important role in adsorption. The adsorbed amount increases as χ_s is increased (solvent–adsorbent interaction decreases, favouring the polymer segments) whereupon a complete reversal of adsorption is observed, i.e. linear polymer adsorbing greater than the corresponding cyclic polymer.

The cross-over effect can be understood since at low molar mass the difference in conformational entropy on adsorption between cyclic and linear polymers favours the adsorption of cyclics; whereas at high adsorbed amount the development of tails increases the adsorption of linear polymers. Since a ring cannot form large tails, it loses proportionally less entropy on adsorption than a linear polymer.

CONCLUSIONS

The results obtained from the adsorption studies of cyclic and linear PDMS from solution are in good qualitative agreement with the theoretical predictions of Cosgrove and coworkers[15]. The theory predicts that under certain physical conditions cyclic polymers adsorb to a greater extent than their linear analogues at low molar mass. However, under different conditions, the reverse behaviour is found. The cyclics can form large loops, but they cannot form long extended tails, which predominate at high molar mass and high adsorbed amounts with linear polymers.

ACKNOWLEDGEMENTS

At the University of York we would like to thank the late Dr D. J. Orrah and Mr T. M. Elsworth for the preparation and characterization of PDMS fractions, and Dr J. H. Clark for the facility of the *FT*i.r. spectrometer. One of us (A.P.) is indebted to the SERC for a Research Studentship. We thank Mr T. C. Kendrick, Dow Corning Ltd, Barry, S. Glamorgan, for providing materials and financial support. We would like to thank Mr C. Prestidge for advice on i.r. techniques, Dr J. Webster for help on the SF programs, and Jan Scheutjens and also the members of the research group for helpful discussions.

REFERENCES

1 Cosgrove, T., Cohen Stuart, M. A. and Vincent, B. *Adv. Colloid Interface Sci.* 1986, **24**, 143
2 Scheutjens, J. M. H. M. and Fleer, G. J. *J. Phys. Chem.* 1979, **83**, 1619; 1980, **84**, 178
3 Cohen Stuart, M. A., Waajen, F. H. M. H., Cosgrove, T., Vincent, B. and Crowley, T. L. *Macromolecules* 1984, **17**, 1825
4 Semlyen, J. A. and coworkers 'Studies of cyclic and linear poly(dimethylsiloxanes) Parts 1–29' *Polymer* 1977–1989
5 Dodgson, K. and Semlyen, J. A. *Polymer* 1977, **18**, 1265
6 Dodgson, K., Bannister, D. J. and Semlyen, J. A. *Polymer* 1980, **21**, 663
7 Higgins, J. S., Dodgson, K. and Semlyen, J. A. *Polymer* 1979, **20**, 553
8 Edwards, C. J. C., Stepto, R. F. T. and Semlyen, J. A. *Polymer* 1982, **23**, 869
9 Edwards, C. J. C., Stepto, R. F. T. and Semlyen, J. A. *Polymer* 1981, **22**, 377
10 Edwards, C. J. C., Stepto, R. F. T. and Semlyen, J. A. *Polymer* 1982, **23**, 865
11 Edwards, C. J. C., Bantle, S., Burchard, W., Stepto, R. F. T. and Semlyen, J. A. *Polymer* 1982, **23**, 873
12 Higgins, J. S., Ma, K., Nicholson, L. K., Hayter, J. B., Dodgson, K. and Semlyen, J. A. *Polymer* 1983, **24**, 793
13 Garrido, L., Mark, J. E., Clarson, S. J. and Semlyen, J. A. *Polym. Commun.* 1985, **26**, 53, 55
14 Burton, D. J., Harris, R. K., Dodgson, K., Pellow, C. J. and Semlyen, J. A. *Polym. Commun.* 1983, **24**, 278
15 van Lent, B., Scheutjens, J. M. H. M. and Cosgrove, T. *Macromolecules* 1987, **20**, 366
16 Dodgson, K., Sympson, D. and Semlyen, J. A. *Polymer* 1978, **19**, 1285
17 Semlyen, J. A. and Wright, P. V. in 'Chromatography of Synthetic Polymers and Biopolymers' (Ed. R. Epton), Ellis Horwood, Chichester, 1977
18 Brebner, K. I., Chahal, R. S. and St-Pierre, L. E. *Polymer* 1980, **21**, 533
19 Ashmead, B. V. and Owen, M. J. *J. Polym. Sci. (A-2)* 1971, **9**, 331