Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Preferential and Total Sorption in the Aminopropyl-Terminated Polydimethylsiloxane/Toluene/Nitromethane System

Gabriela Grigorescu[a]; Silvia Ioan[a]; Crina Cojocaru[b]; Valeria Harabagiu[a]; Bogdan C. Simionescu[c]
[a] "P. Poni" Institute of Macromolecular Chemistry, Jassy, Romania [b] "Al. I. Cuza" University, Jassy, Romania [c] Department of Macromolecules, "Gh. Asachi" Technical University, Jassy, Romania

To cite this Article Grigorescu, Gabriela , Ioan, Silvia , Cojocaru, Crina , Harabagiu, Valeria and Simionescu, Bogdan C.(1997) 'Preferential and Total Sorption in the Aminopropyl-Terminated Polydimethylsiloxane/Toluene/Nitromethane System', Journal of Macromolecular Science, Part A, 34: 3, 533 — 541

To link to this Article: DOI: 10.1080/10601329708014980

URL: http://dx.doi.org/10.1080/10601329708014980

J.M.S.—PURE APPL. CHEM., A34(3), pp. 533-542 (1997)

PREFERENTIAL AND TOTAL SORPTION IN THE AMINOPROPYL-TERMINATED POLYDIMETHYLSILOXANE/TOLUENE/NITROMETHANE SYSTEM

Gabriela Grigorescu[a], Silvia Ioan[a], Crina Cojocaru[b], Valeria Harabagiu[a] and
Bogdan C. Simionescu[c]
[a] "P.Poni" Institute of Macromolecular Chemistry, RO-6600 Jassy, Romania,
[b] "Al. I. Cuza" University, RO-6600 Jassy, Romania,
[c] Department of Macromolecules, "Gh. Asachi" Technical University,
RO-6600 Jassy, Romania

ABSTRACT

The present paper continues our previous studies on solution behaviour of polydimethylsiloxanes with amino end groups. The total and preferential adsorption coefficients for aminopropyl - terminated polydimethylsiloxanes in toluene (solvent)/ nitromethane (nonsolvent) dilute solutions are determined.

INTRODUCTION

The investigation of the physico-chemical properties of macromolecules in mixed solvents is of major importance for a number of reasons: (1) some polymers do not dissolve molecularly in single solvents, but molecular solutions can be obtained in mixed solvents; (2) a certain property of the solvent, a definite value of the second virial coefficient, or a particular value of the refractive index, for instance, is more often found in mixed than in single solvents; (3) such investigations lead to a better knowledge of the respective affinity of each solvent with regard to the macromolecule and of its influence on the molecular dimensions of the polymer.

Polymers in mixed solvents present interesting phenomena; among them, cosolvency and preferential adsorption are notable examples. The preferential adsorption coefficient, λ_1, which defines the affinity of the polymer chain toward one of the solvents, can present peculiar variations with solvent composition [1-13]. The simplest behaviour to be imagined for λ_1 is that the preferentially adsorbed solvent should be the better solvent of the polymer. However, the real situation is more complex. There are numerous examples in which the poor solvent or even a strong precipitant is preferentially adsorbed [1-4, 12-15]. Often, one of the two liquids in the solvent mixture is preferentially adsorbed in a certain range of solvent compositions while the other liquid is adsorbed in the rest of the composition range, thus giving an inversion in the variation of λ_1 [14, 15].

The behaviour of polymers in binary solvents is considerably influenced by the temperature, chemical structure of the polymer chain and the thermodynamic nature of the solvents and of the mixture [16-18]. In some previously published papers [19-21], polydimethylsiloxanes with amino end groups (PDMS-NH_2) in toluene/acetone and toluene/nitromethane mixtures were discussed as concerns the transition concentrations (diluted - semidiluted - concentrated), the influence of solvent quality and temperature on the intrinsic viscosity, the mean perturbed and unperturbed dimensions of the chain, the short-range interactions, the second virial coefficient, the interpenetration and the hydrodynamic penetration function. The crossover region, i.e., the region separating the oligomers from the polymers was considered in detail. Toluene/nitromethane appeared to be a interesting mixture for thermodynamic studies, the first component being one of the most common good solvents for polydimethylsiloxane while the second one acting as a nonsolvent.

To better understand the behaviour of the amino - terminated polydimethylsiloxane/toluene/nitromethane system, the present paper is concerned with the investigation of total and preferential sorption by the polymer in the mentioned solvent mixture.

EXPERIMENTAL PART

The investigated polymers, namely α, ω-bis(3-aminopropyl)-polydimethylsiloxanes (PDMS-NH_2) were obtained by anionic equilibration of octamethylcyclotetrasiloxane with 1,3-bis(aminopropyl)-1,1,3,3-tetramethyl-disiloxane. Samples with number average molecular weights M_n ranging from $0.23 \cdot 10^4$ to 10^5 were synthesized. The M_n were determined by potentiometric titration of terminal amine groups. Polydispersities up to 1.6 were obtained by comparing GPC data (M_w) with M_n values as determined by titration.

The intrinsic viscosities [η] (ml/g) reported here relate to a temperature of 25± 0.01°C in toluene (1)/nitromethane (2) mixtures of different compositions; the values were obtained by using an Ubbelohde suspended-level viscometer and were treated by the Huggins plot. Flow times for the reagent-grade solvent mixtures were in the 90-127 s range. Kinetic energy corrections were found to be negligible. The flow volume of the viscometer was greater than 5 ml, making drainage errors unimportant [22]. The [η] values were accurate to within ± 2%.

The concentration range was from 0.16 to 0.01 g/ml for PDMS-NH_2 (3) of different molecular weights at different compositions of toluene/nitromethane mixture. Since the Huggins coefficients were less than 0.5, chain associations are to be excluded.

A Zeiss interferometer (wavelength of 436 nm) was used for the determination of refractive index increments. The solutions were dialyzed against the pure solvents using regenerated cellulose membranes. A kinetic study of the dialysis process was performed to find out when equilibrium was reached.

RESULTS AND DISCUSSION

Figure 1 shows the viscometric results obtained for the PDMS-NH_2 samples with different molecular weights, at 25°C, as a function of nitromethane volume fraction (ϕ_2) in the toluene/nitromethane mixture. The dependence of [η] *vs.* composition of mixed solvent presents a slight decrease of the slope with increasing nitromethane content in the mixture.

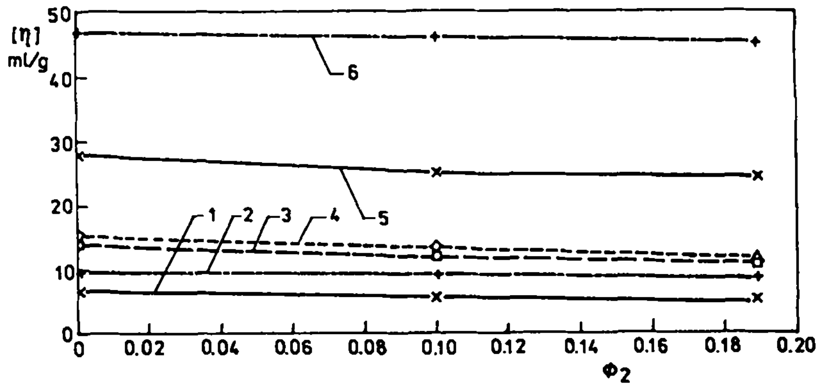

Figure 1. Plots of intrinsic viscosity against binary mixture composition at 25°C for the toluene/nitromethane/ PDMS-NH_2 system. (1) $M_n= 0.53\cdot10^4$; (2) $M_n= 1.27\cdot10^4$; (3) $M_n= 1.66\cdot10^4$; (4) $M_n=2.42\cdot10^4$; (5) $M_n=5\cdot10^4$; (6) $M_n=1\cdot10^5$.

To know the proportion of both liquids in the macromolecular coil as a function of binary solvent composition, the experimental values of the preferential and total sorption coefficients were calculated. The preferential adsorption coefficient, λ_1, was directly accesible from experiments, through interferometry and dialysis equlibrium, according to eq. (1) [23-25]:

$$\lambda_1 = \frac{(dn / dc_3)_\mu - (dn / dc_3)_{\phi_1}}{dn / d\phi_1} \qquad (1)$$

where $(dn/dc_3)_{\phi_1}$ is the refractive index increment of the polymer in the mixed solvent at fixed concentration of the two low molecular weight components in both the polymer solution and solvent mixture, $(dn/dc_3)_\mu$ is the refractive index increment under conditions when all the low molecular weight components have the same chemical potentials in both the polymer solution and solvent mixture, and $dn/d\phi_1$ represents the refractive index increment of the solvent component 1 with respect to the binary solvent mixture of a given composition.

Figure 2 shows the variation of the preferential adsorption coefficient for PDMS-NH_2 in toluene/nitromethane mixture at 25°C, as obtained by differential

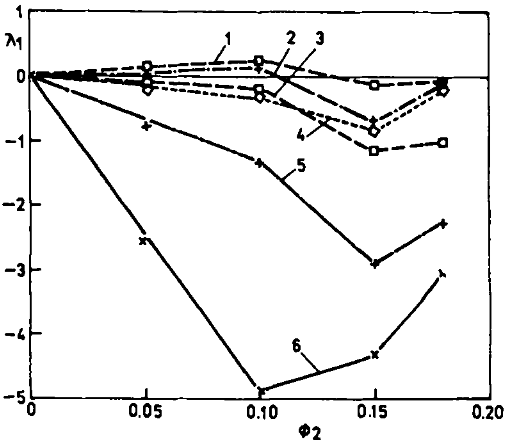

Figure 2. Experimental values of the preferential adsorption coefficient in the toluene/nitromethane binary mixture as a function of the volume fraction of nitromethane (ϕ_2) at 25°C, for PDMS-NH_2 of different molecular weights:
(1) $M_n=0.2 \cdot 10^4$; (2) $M_n=1.27 \cdot 10^4$; (3) $M_n=1.66 \cdot 10^4$; (4) $M_n=2.42 \cdot 10^4$;
(5) $M_n=5 \cdot 10^4$; (6) $M_n=1 \cdot 10^5$.

refractometry and dialysis equilibrium (eq. (1)). The determination of λ_1 was possible in the composition range $0<\phi_2<0.18$ [26]; for $\phi_2>0.18$ polymer precipitation took place. For molecular weights higher than $1.27 \cdot 10^4$ a preferential adsorption of nitromethane for the whole studied composition range is observed. The absolute value of the preferential adsorption of nitromethane with solvent composition increases with increasing the molecular weight; for the $0.2 \cdot 10^4$ molecular weight sample the variation of preferential adsorption coefficient is insignificant ($\lambda_1 \cong 0$). The observed behaviour may be interpreted as being caused by the combined action of toluene and non-associated nitromethane molecules. For the toluene/nitromethane binary solvent mixture, nitromethane clustering breaks down with increasing the toluene content. Also, hydrogen bonds between the amino end groups of PDMS-NH_2 and nitromethane can occur, their importance increasing with decreasing polymer molecular weight. The variation of the preferential adsorption coefficient with the molecular weight for different compositions of the toluene/nitromethane mixture is shown in Figure 3. For high

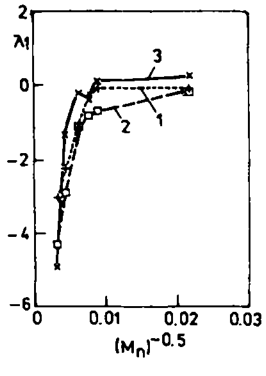

Figure 3. Experimental values of the preferential adsorption coefficient in the toluene/nitromethane binary mixture as a function of polymer molecular weight at different volume fractions of nitromethane (ϕ_2) at 25°C, for PDMS-NH$_2$:
(1) $\phi_2 = 0.82$; (2) $\phi_2 = 0.85$; (3) $\phi_2 = 0.9$.

molecular weight polymer samples, the dependence of the preferential adsorption coefficient on the molecular weight is evident, while for low molecular weights, λ_1 is aproximatively independent on the molecular weight.

The total sorption parameter Y was calculated using equation (2). The interaction parameter B, which is related to the total sorption function Y by the expression proposed by Kurata and Stockmayer [27], can be obtained from viscometric data.

$$Y = \frac{BV_0N_A}{2v_3^2} \tag{2}$$

In eq. (2), B characterizes the polymer - solvent interaction, v_3 is the partial specific volume of the polymer, N_A is Avogadro's number and V_0 is the molar volume of the mixed solvent. For each composition, the parameter B was calculated using the modified Stockmayer-Fixman plot [28, 29] for ternary solvent/solvent/polymer systems (eq. (3)) [28], the condition
$1 < [\eta] / k_\theta M^{1/2} < 1.6$ being valid:

$$\frac{[\eta]}{M^{1/2}} = k_\theta + 0.346\phi_0 BM^{1/2} \tag{3}$$

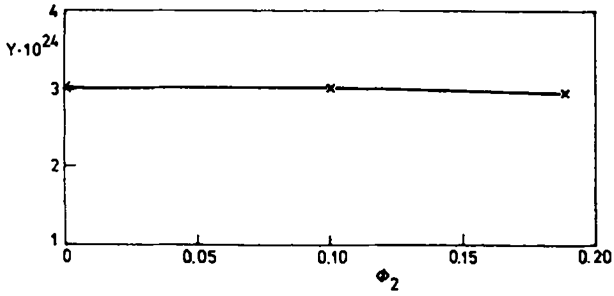

Figure 4. Total adsorption coefficient Y *vs.* nitromethane volume fraction ϕ_2 for toluene/nitromethane/ PDMS-NH_2 system at 25°C.

where k_θ is the constant from the Mark-Houwink equation in the theta solvent, proportional to unperturbed dimensions; ϕ_0 is the Flory constant, i.e., $2.51 \cdot 10^{23}$ [30].

Figure 4 presents the variation of experimental Y values with solvent mixture composition. As known, the total adsorption coefficient is a measure of the excluded volume effect and its behaviour is similar to that of the intrinsic viscosity *vs.* solvent mixture composition.

CONCLUSIONS

The preferential and total sorption coefficients for PDMS-NH_2 in toluene/nitromethane mixture have been measured by refractive index increments and viscometry over the composition range $0<\phi_2<0.18$. The preferential adsorption coefficient for the investigated system was observed to be relatively independent on the molecular weight for low molecular weight samples. The oligodimethylsiloxane presents the same low affinity for both components of the solvent mixture. Our previous studies [20, 21] demonstrated that an unperturbed state is characteristic for polymeric chains with molecular weights up to 10^4, i. e., only the interactions between solvents are important.

Increasing the molecular weight determines a preferential adsorption of nitromethane for all studied compositions, as a result of increasing excluded volume effect with the molecular weight and also the combined action of toluene and non-associated nitromethane molecules. Also, hydrogen bonds between the amino end groups of PDMS-NH_2 and nitromethane could act in the same direction. For the investigated molecular weight domain, once polymer chain length reaches a certain dimension, a dependence between the preferential adsorption of nitromethane and the molecular weight was observed.

A minor influence of the solvent mixture on the the intrinsic viscosity and on the total adsorption coefficient was observed; the values of these parameters are a consequence of the independence of the excluded volume effect in this ternary system on the thermodynamic quality of the solvent mixture.

REFERENCES

1. H. Maillols, L. Bardet and S. Gromb, Eur. Polym. J., 14, 1015 (1978).
2. J. Scornaux and R. V. Leemput, Makromol. Chem., 177, 2721 (1976).
3. A. Horta, D. Radic and L. Gargallo, Macromolecules, 22, 4267 (1989).
4. A. Horta, L. Gargallo and D. Radic, Macromolecules, 23, 5320 (1990).
5. G. Grigorescu, S. Ioan and B. C. Simionescu, Polym. Bull., 31, 123 (1993).
6. G. Grigorescu, S. Ioan and B. C. Simionescu, Eur. Polym. J., 32, 851 (1996).
7. C. M. Gomez, R. Garcia, V. Soria and A. Campos, Colloid Polym. Sci., 271, 30 (1993).
8. P. Chatterjee and S. Bagchi, J. Phys. Chem., 95, 3311 (1991).
9. Z. Tuzar, O. Prochazka and P. Kratochvil, Eur. Polym. J., 17, 87 (1991).
10. J. Vavra, Colloid. Polym. Sci., 271, 480 (1993).
11. P. Auroy and L. Auvray, Langmuir, 10, 225 (1994).
12. L. Gargallo and D. Radic, Adv. Colloid Interface Sci., 21, 1 (1984).
13. C. I. Simionescu, S. Ioan, M. Bercea and B. C. Simionescu, Eur. Polym. J., 29, 183 (1993).
14. R. M. Masegosa, M. G. Prolongo, I. Hernandez-Fuentes and A. Horta, Macromolecules, 17, 1181 (1984).

15. I. A. Katime, L. Gargallo, D. Radic and A. Horta, Makromol. Chem., 186, 2125 (1985).

16. A. Dondos and H. Benoit, Makromol. Chem., 133, 119 (1970).

17. P. Munk, M. T. Abijaoude and M. E. Halbrook, J. Polym. Sci., Polym. Phys, 16, 105 (1978).

18. L. Gargallo, D. Radic and I. Katime, Eur. Polym. J., 16, 383 (1980).

19. G. Grigorescu, S. Ioan, V. Harabagiu and B. C. Simionescu, Rev. Roum. Chim., in press.

20. G. Grigorescu, S. Ioan, V. Harabagiu and B. C. Simionescu, Macromol. Reports, A33, 163 (1996).

21. G. Grigorescu, S. Ioan, V. Harabagiu and B. C. Simionescu, Eur. Polym. J., submitted.

22. W. O. Baker, C. S. Fuller and H. Heiss jr., J. Am. Chem. Soc., 63, 214 (1941).

23. J. G. Kirkwood and R. J. Goldberg, J. Chem. Phys., 18, 541 (1950).

24. W. H. Stockmayer, J. Chem. Phys., 18, 58 (1950).

25. R. H. Ewart, C. P. Roe, P. Debye and J. R. McCartney, J. Chem. Phys., 14, 687 (1946).

26. H. G. Elias and H. G. Buhner, in Polymer Handbook, second edition, J. Brandrup and E. H. Immergut, Eds., (1974) IV-157.

27. M. Kurata and W. H. Stockmayer, Fortschr. Hochpolym. Forsch., 3, 196 (1963).

28. T. Spychaj, D. Lath and D. Berek, Polymer, 20, 437 (1979).

29. H. Yamakawa, Modern Theory of Polymer Solutions, (1971), Harper&Row, New York.

30. B. H. Zimm, Macromolecules, 13, 592 (1980).