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ORIGINAL CONTRIBUTION

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The polymerisation of aqueous sodium undecenoate mesophases

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Abstract Sodium 10-undecenoate is a polymerisable surfactant having a double bond in the ω position of its chain. This surfactant has been polymerised by McGrath, both in lamellar and hexagonal mesophases by thermal and photochemical initiation, and she obtained relatively low conversions. She could not obtain the polymerisation kinetics. We have polymerised both liquid crystals by irradiation by γ-rays, and we obtained higher conversions: $91.6 \pm 0.7\%$ in 50 wt% of surfactant in water (hexagonal mesophase), while McGrath obtained 56% by thermal and 20.6% by photochemical polymerisation; and a maximum of 59.5% in 75 wt% of surfactant in water (lamellar liquid crystal). McGrath obtained conversion values of 24% (thermal initiation) and 19.2% (photochemical initiation) for this mesophase. We could not obtain the polymerisation kinetics of the 50 wt% sample. Even at the lowest irradiation dose the conversion rendered the maximum value. The 75% sample showed a measurable polymerisation increase with γ-radiation dose until 60 kGy, but a large decomposition was observed at 80 kGy. This decomposition, caused by an excess of radiation, is not exceptional. The Fourier transform IR study of the different kinds of water in the system (bulklike water, water related to surfaces and water molecules trapped in the interstices of the microstructures) indicates that there was no significant transformation of the structure during the irradiation; the values of the nonirradiated liquid crystal remained almost unchanged.

Keywords Surfactant polymerisation · Sodium undecenoate · Liquid-crystal polymerisation · Mesophases

Introduction

Surfactant molecules with chemically active groups have received increased attention in recent years. Since these materials can often be polymerised or oligomerised, a wide range of uses can be foreseen. Polymerisable surfactants can be polymerised to yield polysoaps, which can form hydrophobic microdomains having properties similar to surfactant micelles [1, 2]. They may also be copolymerised with water-soluble or water-insoluble monomers [3, 4, 5]. The polymerised structures may be micelles [6, 7], vesicles [8, 9, 10], monolayers [11, 12], bilayers [13, 14], liquid crystals [15, 16], and microemulsions [17, 18, 19].

The polymerisation of amphiphilic monomers when they form stable aggregation structures enables materials having interesting properties to be obtained with potentially specific applications, such as the production of membranes with extremely well defined pores [6, 15, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30].

Sodium 10-undecenoate [SUD, $CH_2=CH-(CH_2)_8COONa$] is a polymerisable surfactant having a double bond in the ω position of the chain. It can be polymerised to produce low molecular weight SUD oligomers after irradiation by γ-rays [21, 31, 32, 33, 34] or by chemical methods [15, 33, 35]. The potassium salt was employed in copolymerisation with methyl methacrylate in microemulsions [34].

This surfactant has been polymerised by McGrath [35], both in lamellar and hexagonal mesophases by thermal and photochemical initiation. She obtained relatively low conversions and could not follow the polymerisation kinetics. We polymerised both liquid crystals by irradiation by γ-rays, obtaining higher conversions: $82.3 \pm 0.7\%$ in 50 wt% of surfactant in water (hexagonal mesophase), while McGrath obtained 34.5% by thermal and 20.6% by photochemical polymerisation; also 19% (thermal) and 19.2% (photochemical) conversion in 75 wt% of surfactant in water (lamellar liquid crystal). We could not obtain the polymerisation kinetics of the 50 wt% sample. Even at the lowest irradiation dose the conversion was almost the maximum value. The 75 wt% sample showed a measurable polymerisation increase with γ-radiation dose until 60 kGy, but a large decomposition was observed at 80 kGy. This decomposition was caused by an excess of radiation and it is not exceptional.

Experimental

SUD was from Aldrich. Samples were prepared by weighing SUD and water in glass ampoules. These ampoules were closed with rubber stoppers and placed into a water bath at 60 °C for 2 days where they were frequently shaken to homogenise the contents. Then the samples were frozen with liquid air and degassed by the freeze–pump–thaw technique to remove as much oxygen (a polymerisation inhibitor) as possible. Then the ampoules were flame-sealed while still under vacuum. Two series of samples were studied, one with 50 wt% of SUD, which corresponds to a hexagonal liquid crystal, and the other with 75 wt% of SUD, which was a lamellar liquid crystal [35]. The samples were irradiated at 11.2 kGy h^{-1} with γ-rays for different time periods at room temperature. The polymerisation progress was monitored as a function of time by stopping the irradiation of different ampoules with samples of the same composition at the desired times. Irradiation was performed at the Irradiation Plant in the Ezeiza Atomic Center of the Comisión Nacional de Energía Atómica de la República Argentina.

Aliquots of the irradiated samples were desiccated up to constant weight to obtain the water content. Then these samples, and the nondried ones, were studied by Fourier transform (FT)-IR spectroscopy.

FT-IR studies were performed using a Nicolet FT-IR Nexus 470 spectrophotometer. Liquid-crystal samples were sandwiched between IRTRAN-4 windows as capillary films. Dried samples were studied in KBr pills. The state of water in the samples was studied in the 2,700–3,800-cm^{-1} range. The water bands were superimposed on those of symmetric and asymmetric modes of methyl and methylene groups, and that of the asymmetric mode of the $-CH=CH_2$ group at 3,080 cm^{-1}. The polymerisation was verified by comparing the decrease of the 1,003-cm^{-1} peak area (=C-H bending) with that of the peak at 721 cm^{-1} [$(CH_2)_{n>4}$ deformation], which was invariant when samples were irradiated. All peaks were deconvoluted using the Peakfit program.

The samples were observed using a polarised light microscope prior to and after polymerisation to detect texture changes. Mean values and variances were computed with the minimum variance linear unbiased method [36] and the Student t function was employed to compute the error intervals. The confidence level was 0.90. Errors of derived data were computed with the error expansion method.

Results

The state of water

The deconvoluted FT-IR spectrum of the O–H stretching (ν_{OH}) absorption of water in nonpolymerised samples having 50 wt% and 75 wt% of surfactant are shown in Fig. 1. It has been reported that the broad OH stretching water band in a surfactant system is a combination of three bands that correspond to three different "types of water" [37, 38, 39, 40, 41]. The band with the maximum absorption wave number at $3{,}290 \pm 20$ cm^{-1} corresponds to "free" or "bulklike water"; while that at $3{,}490 \pm 20$ cm^{-1} belongs to "interfacial" water, and that at $3{,}610 \pm 10$ cm^{-1} is due to "trapped water" [41]. These three types of water in surfactant liquid-crystalline systems have been reported in the literature [42, 43, 44, 45].

The number of molecules of each type of water per surfactant molecule ($R = n_W/n_S$, where n_W and n_S are the numbers of molecules of water and surfactant in the sample, respectively) were determined as a function of the percentage of polymerisation, in samples with 50 and 75 wt% of SUD. The average values are shown in Table 1. No significant changes in the amount of each type of water were detected as a function of the degree of polymerisation. This means that the liquid-crystal structure did not significantly change with polymerisation.

Polymerisation

The observation with a polarised light microscope of samples before and after polymerisation showed typical textures of hexagonal (50 wt% of SUD) and lamellar (75 wt% of SUD) mesophases, which did not change with polymerisation.

The reference peak, which is almost invariant with irradiation, in a dried sample initially having 75 wt% of SUD [721 cm^{-1}, $(CH_2)_{n>4}$ deformation] is shown in Fig. 2. The bands between 1,050 and 900 cm^{-1} in a dried polymerised sample of lamellar liquid crystal are shown in Fig. 3. The samples were desiccated because the

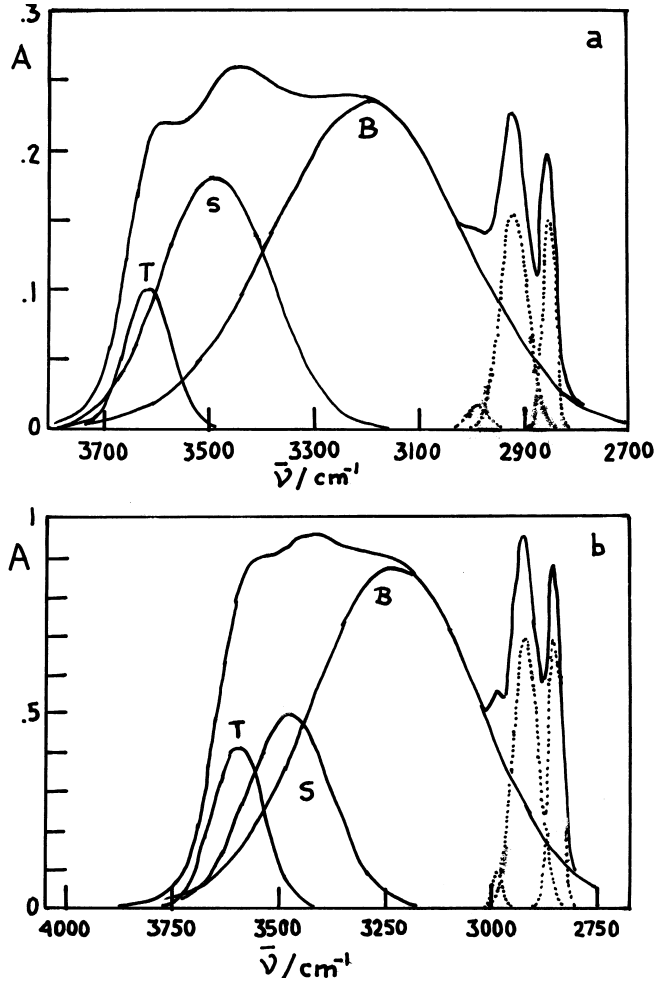

Fig. 1 Deconvoluted Fourier transform IR spectrum of the O–H stretching (ν_{OH}) absorption of water in nonpolymerised samples having a 50 wt% and **b** 75 wt% of sodium 10-undecenoate (*SUD*). Bulklike water (*B*), water related with surfaces (*S*), trapped water (*T*)

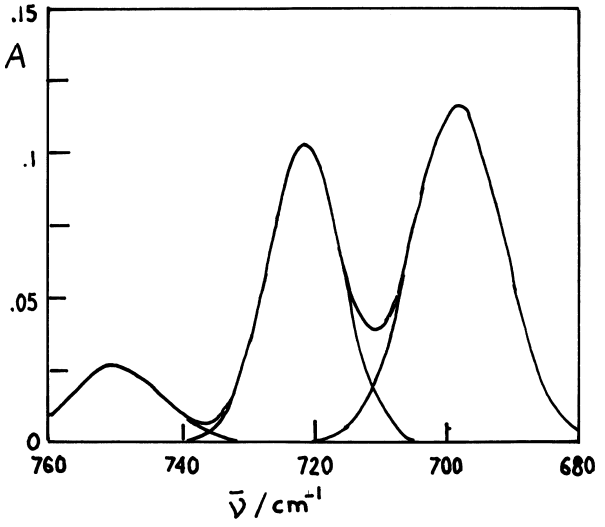

Fig. 2 Reference peak to determine the SUD degree of polymerisation in a dried sample initially having 75 wt% of SUD. 721 cm^{-1}, $(CH_2)_{n>4}$ deformation

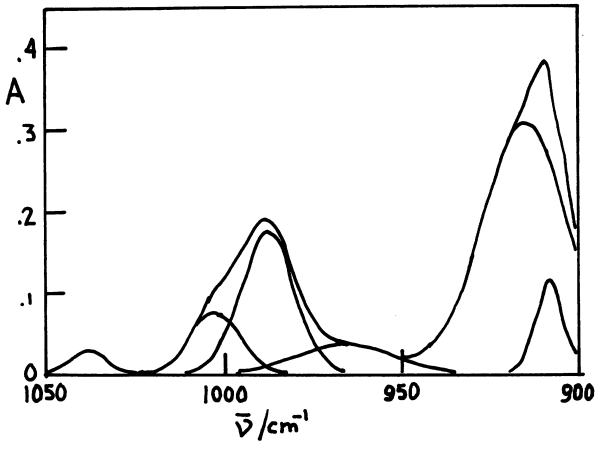

Fig. 3 Bands between 1,050 and 900 cm^{-1} in a dried polymerised sample of lamellar liquid crystal, related to the nonpolymerised vinyl group. The intensity of the peak at 1,003 cm^{-1} decreases with increasing conversion

interaction of the double bond with water by hydrogen bonding generates difficulties in the determination of the degree of polymerisation. This problem was also found in other polymerised surfactants [46].

The dependence of the degree of polymerisation with time for the hexagonal mesophase (50 wt%) is shown in Fig. 4. This system rapidly reached a degree of polymerisation of about 83%. At the minimum irradiation dose (10 kGy) the conversion was 70%. McGrath reported a degree of ionisation of 34.5% by thermal initiation and in 15 days, and 20.6% by photochemical initiation [35].

Table 1 Average values of water molecules per surfactant molecule, *R*, in sodium 10-undecenoate (SUD) liquid crystals

% SUD	R_{bulk}	$R_{surface}$	$R_{trapped}$
50 (hexagonal)	7.46 ± 0.34	3.29 ± 0.22	0.69 ± 0.13
75 (lamellar)	2.81 ± 0.10	0.688 ± 0.073	0.312 ± 0.037

The dependence of the degree of polymerisation with time for the lamellar liquid crystal is shown in Fig. 5. The point at 7.14 h (18.1% polymerisation) was omitted. It indicates substantial decomposition by excessive irradiation.

The dependence of the inverse of the remaining nonpolymerised monomer [1/(100−%PD)] with time (*t*, in hours) is shown in Fig. 6, showing that the

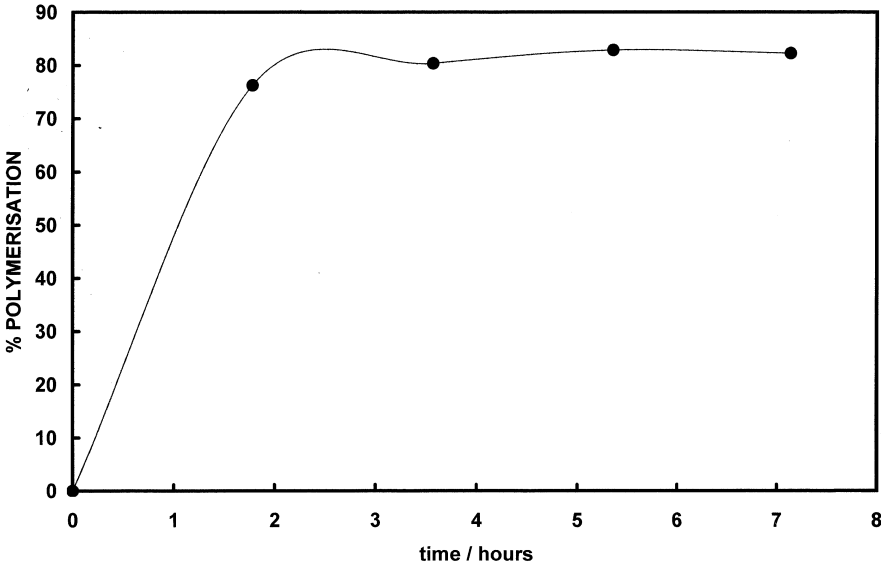

Fig. 4 Conversion of SUD in water at 50 wt% (hexagonal liquid crystal) by γ radiation at 11.2 kGy h^{-1} as a function of time of exposure

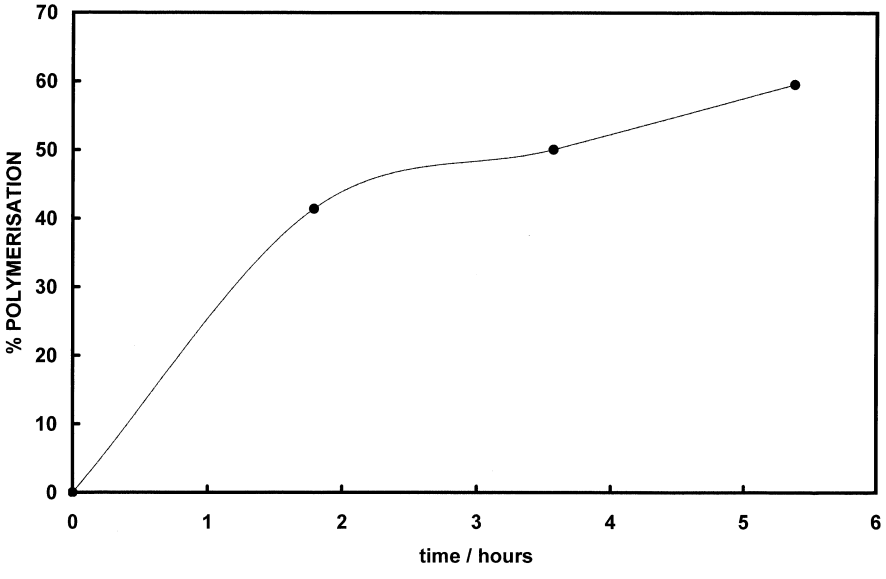

Fig. 5 Conversion of SUD in water at 75 wt% (lamellar liquid crystal) by γ radiation at 11.2 kGy h^{-1} as a function of time of exposure. The point at 7.14 h exposure was omitted

polymerisation follows second-order kinetics. The maximum degree of polymerisation was 59% and the last point was omitted because there was decomposition of the polymer owing to the excessive irradiation. The equation of the least-squares fitting is

$$1/(100 - \%\mathrm{PD}) = (0.00263 \pm 0.00064)t + 0.0109 \pm 0.0022,$$

with the correlation coefficient $r = 0.9864$, giving a second-order kinetic constant of $k = (0.00263 \pm 0.00064)$ $(100-\%\mathrm{PD})^{-1}$ h^{-1}.

Degrees of polymerisation of 19% by thermal and 19.2% by photochemical initiation were reported in the literature; the kinetics of the process could not be followed [35].

Discussion

The difference between results of polymerisation with γ radiation and the hydrosoluble initiator may be explained by the difference in accessibility of the polymerisable vinyl groups to the initiator.

The π electrons of the vinyl group have some affinity to the water, and may form hydrogen bonds with water protons [47, 48, 49, 50, 51, 52]. Then the

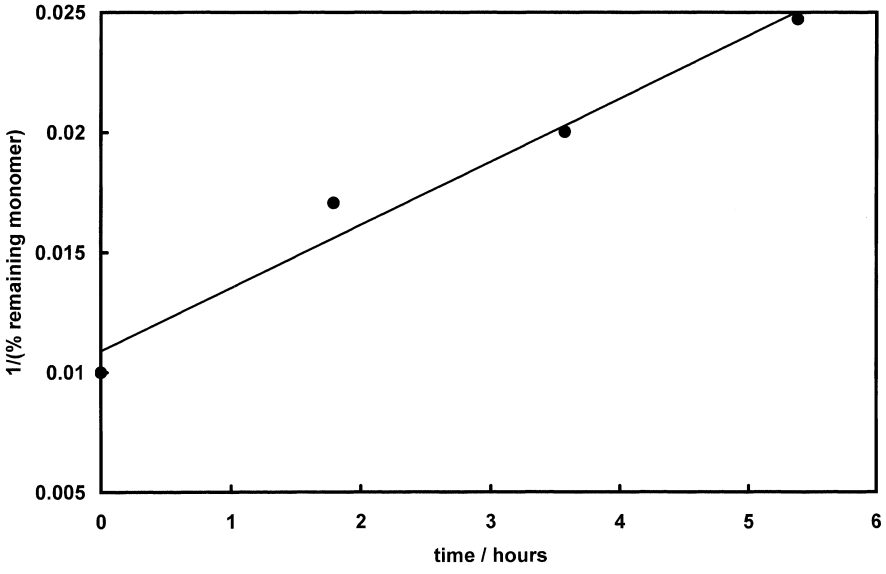

Fig. 6 The inverse of the percentage of SUD monomer in water at 75 wt% (lamellar liquid crystal) not polymerised by γ radiation at 11.2 kGy h^{-1} as a function of time of exposure. The point at 7.14 h exposure was omitted

double bond has a tendency to remain at the surface of the long wormlike micelles forming the hexagonal liquid crystal, in contact with water. It is impossible to obtain these wormlike micelles with their surface completely covered by the hydrophilic head groups. Methyl and methylene groups in direct contact with water must compose a fraction of the surface. Since the chains are in a liquidlike state [53], some of them are folded exposing a part of the chain to water, whilst others are extended inside the micelle hydrocarbon core. As an average, about four carbon atoms per chain are exposed to water in micelles [54, 55, 56, 57, 58, 59, 60, 61]. In the SUD–water system, this quantity amounts to 36% of the total number of carbon atoms of the chains. Because of the affinity of the double bonds to water, it may be supposed that this quantity is composed of vinyl groups that are directly exposed to the water-soluble initiator. Taking into account some portion of the surface occupied by the methylene groups adjacent to the vinyl ones, we can explain the conversion obtained by McGrath (34.5%) [35]. The hydrosoluble initiator does not initiate the double bonds in the extended chains, which are in the hydrophobic core, distant from the water, but they are exposed to the γ-rays, giving the high conversion found in this work (83%).

In the lamellar mesophase, a larger proportion of the aggregates–water interface is occupied by the polar head-groups and the proportion of $-CH=CH_2$ groups in contact with water is much lower than in the hexagonal mesophase (Fig. 7). The 19% of conversion obtained by McGrath [35] may be the proportion of vinyl groups at the interface in the lamellar mesophase. This leads to about two carbon atoms of the chain being exposed to water, half the amount for the hexagonal liquid crystal, caused by the close packing of the surfactant chains in the lamellae.

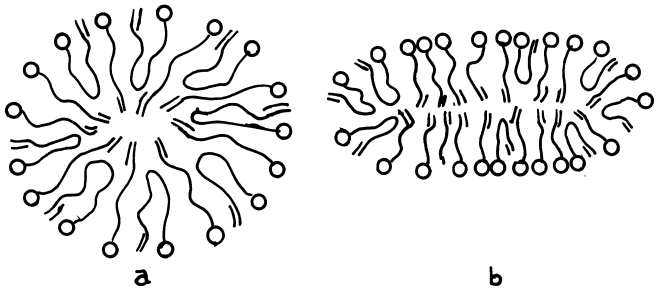

Fig. 7 Localisation of the vinyl groups of SUD in **a** hexagonal and **b** lamellar mesophases

McGrath [35] obtained a conversion of 80% by thermal polymerisation in a monomer solution of SUD (below the critical micelle concentration) in which all the vinyl groups were in contact with water. This fact reinforces the interpretation that the difference in conversion is due to the exposure of the polymerisable groups to the initiator, which in turn depends on the structure of the aggregates. Since the structure of the aggregates does not change during polymerisation, once the exposed vinyl groups are polymerised, the other double bonds remain trapped in the hydrophobic portion of the aggregate, unattainable to the water-soluble initiator. This explains why McGrath was unable to increase the conversion of the hexagonal mesophase even after a 15-day-long experiment.

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References

1. Tuin G, Candau F, Zana R (1998) Colloids Surf A 131:303
2. Laschewsky A (1995) Adv Polym Sci 124:1
3. Renoux D, Selb J, Candau F (1994) Prog Colloid Polym Sci 97:213
4. Volpert E, Selb J, Candau F (1996) Macromolecules 29:1452
5. Chang Y, McCormick CL (1993) Macromolecules 26:6121
6. Paleos CM, Hristiades C, Evangelatos GP, Dias P (1982) J Polym Sci Polym Chem Ed 20:2565
7. Nagai N, Ottishi Y, Inaba H, Kudo SJ (1985) J Polym Sci Polym Chem Ed 23:1221
8. Kunitake T, Nagai M, Yanangi H, Takarabe K, Nakashima N (1984) J Macromol Sci Chem A 21:1237
9. Kusumi A, Singh M, Tirrell DA, Oehme G, Singh A, Samuel NKP, Hyde JS, Regen SL (1983) J Am Chem Soc 105:2975
10. Chung Y-C (1997) Bull Korean Chem Soc 18:1041
11. Laschewsky A, Ringsdorf H, Schmidt G, Schneider J (1987) J Am Chem Soc 109:788
12. Goettgens BM, Tillmann RW, Radmacher M, Gaug HE (1992) Langmuir 8:1768
13. Suh J, Shin S, Shim H (1997) Bull Korean Chem Soc 18:190
14. Kunitake T, Nakashima N, Kunitake M (1989) Macromolecules 22:3544
15. Thundathil R, Stoffer JO, Friberg SE (1980) J Polym Sci Polym Chem Ed 18:2629
16. Sisson T, Srisiri W, O'Brien DF (1998) J Am Chem Soc 120:2322
17. Full AP, Puig JE, Gron LU, Kaler EW, Minter JR, Mourey TH, Texter J (1992) Macromolecules 25:5157
18. Puig JE, Corona-Galván S, Maldonado A, Schulz PC, Rodríguez BE, Kaler EW (1990) J Colloid Interface Sci 137:308
19. Li TD, Gan LM, Chew CH, Teo WK, Gan LH (1996) Langmuir 12:5863
20. Paleos CP, Dais P (1984) In: Vhapori C (ed) Recent advances in liquid crystalline polymers. Elsevier, London, pp
21. Larrabee CE, Sprague ED (1979) J Polym Sci Polym Lett Ed 17:749
22. McGrath KM, Drummond CJ (1996) Colloid Polym Sci 274:316
23. McGrath KM, Drummond CJ (1996) Colloid Polym Sci 274:399
24. Fendler HF, Tundo P (1984) Acc Chem Res 17:3
25. Friberg SE, Yu B, Campbell GA (1990) J Polym Sci Polym Chem Ed 28:3575
26. Friberg SE, Yu B, Ahmed AU, Campbell GA (1993) Colloids Surf A 69:234
27. Gan LM, Chew CH, Yeoh KM, Kohll R (1990) J Colloid Interface Sci 137:597
28. Chew CH, Gan LM, Ong LH, Zhang K, Li TD, Loh TP, MacDonald PM (1997) Langmuir 13:2817
29. Wu J, Harwell JH, O'Rear EA (1987) Langmuir 3:531
30. Anderson DM, Ström P (1984) In: El Nokadi MM (ed) Polymer association structures: microstructures and liquid crystals. ACS symposium series 384. American Chemical Society, Washington, DC, chap 13
31. Paleos CM, Stassinopoulou CI, Malliaris A (1983) J Phys Chem 87:251
32. Denton JM, Dueker DC, Sprague ED (1993) J Phys Chem 97:756
33. Gambogi RJ, Blum FD (1990) J Colloid Interface Sci 140:525
34. Raj WRP, Sesthav M, Cheung HM (1992) Langmuir 8:1931
35. McGrath KM (1996) Colloid Polym Sci 274:499
36. Mandel J (1964) Statistical analysis of experimental data. Interscience, New York, pp 134–137
37. Walfren AK (1968) In: Covington AK, Jones P (eds) Hydrogen bonded solvent systems. Taylor and Francis, London, pp
38. Tso TL, Lee ECK (1985) J Phys Chem 89:1612
39. Kawai T, Umemura J, Takenata T, Kodama M, Seki S (1985) J Colloid Interface Sci 103:56
40. MacDonald H, Bedwell B, Gulari E (1986) Langmuir 2:704
41. Jain TK, Varshney M, Maitra A (1989) J Phys Chem 93:7409
42. Casillas N, Puig JE, Olayo R, Hart TJ, Franses EI (1989) Langmuir 5:384
43. Czarniecki K, Jaich A, Janick JM, Rachwalska M, Janick JA, Krawczyc J, Otnes K, Volino F, Ramasseul R (1983) J Colloid Interface Sci 92:358
44. Puig JE, Soltero JFA, Franses EI, Torres LA, Schulz PC (1996) In: Chattopadhyay AK, Mittal KL (eds) (1996) Surfactants in solution. Dekker, New York, pp
45. Schulz PC (1998) J Therm Anal 51:135
46. Rodríguez JL, Soltero JFA, Puig JE, Schulz PC, Espinoza-Martínez ML, Pieroni O (1999) Colloid Polym Sci 277:1215]
47. Furutaka S, Ikawa S-J (1998) J Phys Chem 108:1347
48. Furutaka S, Ikawa S-J (1998) J Phys Chem 108:5159
49. Goldman M, Crisler RO (1958) J Org Chem 23:751
50. Oki M, Iwamura H (1960) Bull Chem Soc Jpn 33:717
51. Rablen PR, Lockman JW, Jorgensen WL (1998) J Phys Chem A 102:3782
52. Atwood JL (1991) Nature 349:683
53. Stigter D (1967) J Colloid Interface Sci 23:379
54. Clifford J, Pethica BA (1965) Trans Faraday Soc 61:182
55. Clifford J (1965) Trans Faraday Soc 61:1276
56. Stigter D (1974) J Phys Chem 78:2480
57. Muller M, Pellerin JM, Chen WW (1972) J Phys Chem 76:3012
58. Drakenberg T, Lindman B (1973) J Colloid Interface Sci 44:184
59. Walker T (1973) J Colloid Interface Sci 45:372
60. Griffith GM, Dehlinger PH, Van SP (1974) J Membr Biol 15:159
61. Ekwall P, Mandell L, Solyom P (1971) J Colloid Interface Sci 35:519