Polymerization of MAA in the presence of glycidoxypropyl functionalized polydimethylsiloxanes (VI and VII)

PDMS - PMAA copolymers (VIII and IX) were obtained by radical polymerization of MAA initiated by BP in the presence of functional polymers VI and VII (Table II).

The reaction was performed in toluene (Total conc., 30%), under N_2, by maintaining the mixture for 9 hours at 80°C in sealed ampoules. After dilution with methanol, the copolymers were separated by precipitation in water and were purified by extraction with petroleum ether.

RESULTS AND DISCUSSION

Functional hydroxypropyl and glycidoxypropyl polydimethylsiloxanes were used in two different manners to synthesize hydrophobic - hydrophilic copolymers containing poly(methacrylic acid) or poly(N-vinylpyrrolidone) sequences.

First, hydroxypropyl terminated polydimethylsiloxanes of different molecular weights were converted into macromolecular azo initiators by solution polycondensation with equimolecular amounts of ACVC. These products are efficient initiators (the activation energy for the initiation of bulk radical polymerization of methyl methacrylate was found to be 143.1 KJ/mol) for the polymerization of usual vinyl monomers[11-13].

As it can be seen from Table I, variation of the monomer/azo group feed ratio or of the molecular weight of siloxane sequences in macromolecular azo initiators results in varying the vinyl unit/Si-O unit molar ratio in copolymers.

^{1}H-NMR spectra of the copolymers allow the estimation of siloxane and vinyl proportion in the copolymers.

The method leads to ABA or $(AB)_n$ type block copolymers, depending on the termination reaction of the vinyl monomer radical polymerization. Their solubilities depend on the relative proportion of the hydrophobic (siloxane) and hydrophilic (polyvinyl) sequences in the block copolymers.

Second, PDMS - PMAA copolymers were obtained (Table II) by radical polymerization of MAA in the presence of glycidoxypropyl functionalized PDMSs (VI and VII), at 80°C, in toluene. Simultaneously, a reaction between the carboxylic groups and epoxy rings takes place in the mentioned conditions leading to

$$CH\text{-}CH_2 + HOOC\text{-} \quad \rightarrow \quad \underset{\text{VIII, IX}}{-CH\text{-}CH_2\text{-}OH}$$
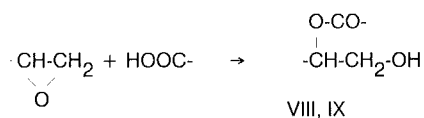
copolymer structures VIII and IX presented in Scheme II.

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CONTRIBUTION OF BLOCK COPOLYMERS TO THE CONTROL OF POLYMERIC SURFACES

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Dedicated to Professor G. Smets on the occasion of his 75th birthday

ABSTRACT

Diblock copolymers of polystyrene and polydimethylsiloxane, and polystyrene end-capped with a fluorinated group have been prepared by anionic polymerization. Polymethylmethacrylate end-capped with the same fluorinated group has been synthesized by a telomerization technique. Surface activity of all these compounds has been studied in solution by tensiometry and in a polymeric matrix by various methods : XPS and measurements of wettability and contact angle. The relative interactions of the dispersion medium with each component of the additive are of a prime importance in the control of the surface energy.

INTRODUCTION

Structure and properties of polymeric surfaces are known to have a strong impact on the technologies of many industrial processes. Surface tension and wetting are important to the manufacture of coatings, films and fibres. They determine practical characteristics, such as friction, permeability, gloss, corrosion, surface electrostatic charging, cellular recognition and biocompatibility.

In this respect, hydrophilic modification of an apolar polymer is most desirable to improve adhesion to polar compounds (e.g. in multilayer composites), wetting and coating by inks, varnishes and paints, and antistatic properties. Similarly, hydrophobic modification of polar polymers is effective in improving water repellency and frictional properties.

Several techniques can be used to permanently modify the surface properties of solid organic polymers : chemical and photochemical reactions, thermal treatments, plasma and ion-beam modifications (1). Low molecular weight fluorinated compounds and silicones have also been used to decrease the polarity of organic materials. Due to their very low surface energy and their immiscibility to the polymeric matrix, these additives diffuse to the surface and decrease the local polarity (1). The surface modification is however not permanent because of the progressive loss of the additive by exudation.

For the last ten years, block and graft copolymers have drawn an increasing attention because of a unique ability to modify polymeric surfaces and interfaces.

When a polymeric matrix is added with a copolymer comprising a component miscible to the matrix and a second immiscible component of a low surface energy, the surface structure is usually different from that of the bulk. This effect results from the surface accumulation of the low surface tension part of the copolymer. The surface modification is observed when only a few percent of a suitable block or graft copolymer are used. Moreover, the matrix miscible component of the copolymer can act as an anchoring partner and ensure the permanency of the surface modification (2,3).

We wish to report in this paper a preliminary study of the surface modification of polystyrene (and polymethyl methacrylate, PMMA) by two-component polymeric additives. Purposely, poly(styrene-b-dimethylsiloxane) have been synthesized (16, 17), and polystyrene (and PMMA) chains have been selectively capped at one end by a fluorinated group ($-C_6F_{13}$). The latter additives are nothing but diblock copolymers whose length of the low surface energy component has been limited to a few constitutive units (CF_2).

EXPERIMENTAL

Synthesis and characterization of two-component additives

A series of poly(styrene-b-dimethylsiloxane) copolymers [P(S-b-DMS)] was prepared by sequential anionic polymerization of styrene and hexamethyl cyclotrisiloxane (D_3) (eqs 1 and 2) (4). Styrene polymerization was first initiated by s-BuLi in toluene at 0°C; temperature was then raised up to room temperature for 4 hours. D_3 and dry tetrahydrofuran (THF) were successively added to living polystyryl chains and the second polymerization step was carried out at 40°C for 4 hours.

The reaction medium was deactivated by acidified methanol and the copolymer was precipitated into methanol, filtered and dried under vacuum.

$$(1)$$

$$(2)$$
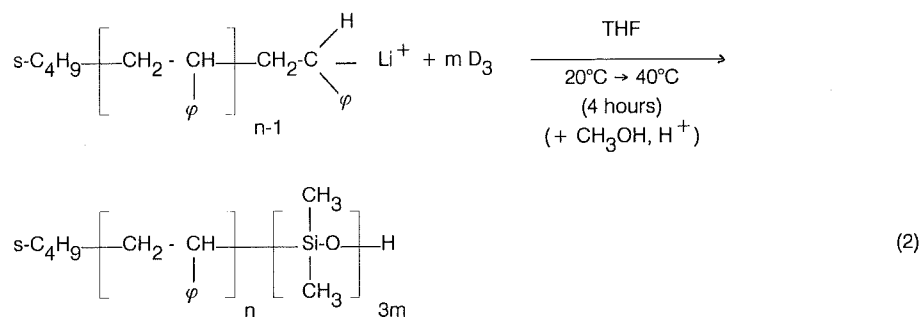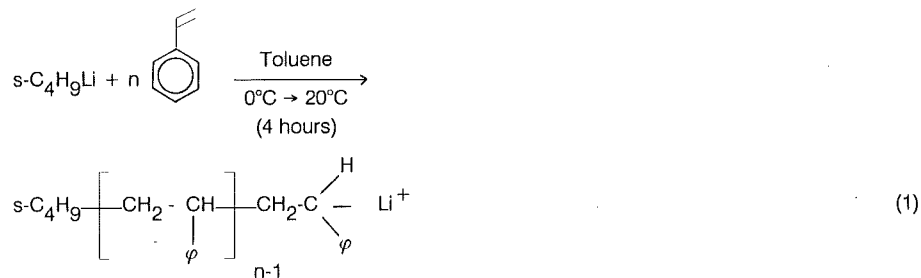
Molecular weight of each block was predetermined by the molar monomer to initiator ratio. Polystyrene blocks and block copolymers were characterized by size exclusion chromatography (SEC) and ^{1}H NMR spectroscopy, as summarized in Table I.

TABLE I.

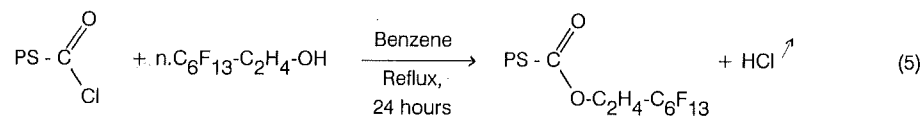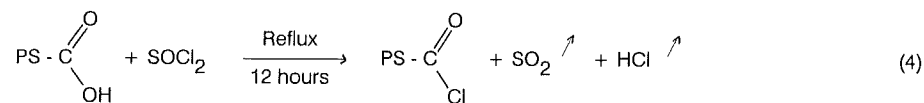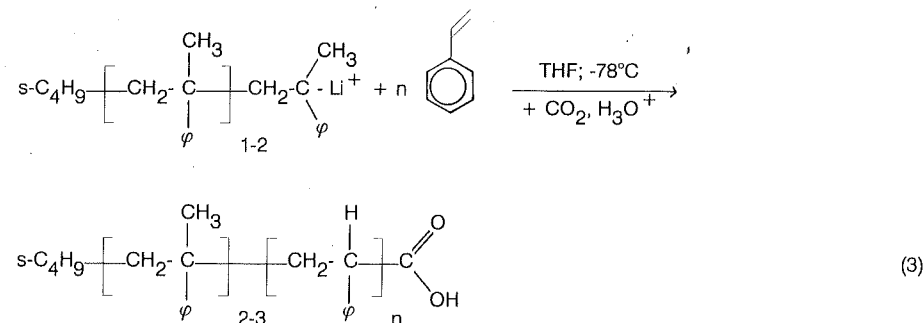Molecular characteristics of the synthesized P(S-b-DMS) copolymers.

Sample	$\overline{M}_n$(PS)[1]	wt % (DMS)[2]	$\overline{M}_n$ (PDMS)[3]	$\overline{M}w/\overline{M}_n$
S 1	5,400	38	3,300	1.4
S 2	12,000	35	6,500	1.3
S 3	19,000	41	13,000	1.3
S 4	35,000	42	25,000	1.5
S 5	13,000	8	1,100	1.2
S 6	10,000	19	2,300	1.3
S 7	13,000	64	23,000	1.7

[1] from SEC using polystyrene standards
[2] by ^{1}H NMR spectroscopy
[3] calculated from $\overline{M}_n$ (PS) and copolymer composition.

The second family of additives was prepared as follows. The living anionic polymerization of styrene was initiated by a premixture of s-BuLi and a few α-methylstyrene units in THF at -78°C for 1 hour. Living polystyryl anions were deactivated by anhydrous CO_2 and precipitated in acidified methanol.

The final ω-carboxylic acid PS was filtered, dried under vacuum and then converted to the acid chloride form by reaction with refluxing $SOCl_2$ for 12 hours. Acid chloride end-groups were esterified by $n.C_6F_{13}$-C_2H_4OH in refluxing benzene for 24 hours.

$$(3)$$

$$(4)$$

$$(5)$$

ω-C_6F_{13} polystyrene samples were recovered by precipitation in methanol, filtration and drying under vacuum. They were characterized by SEC, IR, ^{19}F NMR and elemental analysis. Table II summarizes the molecular characteristics of these polymers.
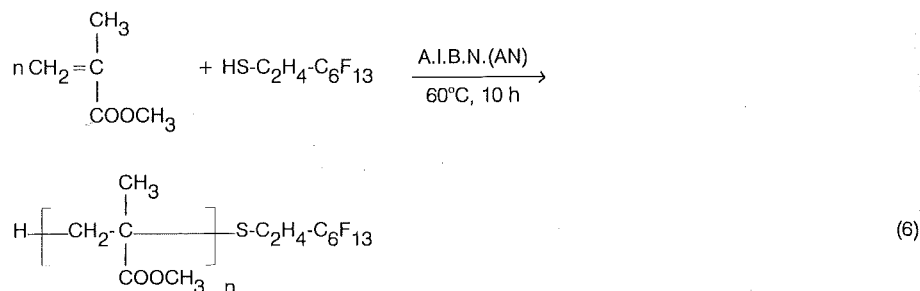
TABLE II.

Molecular characteristics of ω-C_6F_{13} polystyrene samples.

Sample	$\overline{M}_n$[1]	Functionality[2]	$\overline{M}w/\overline{M}_n$
SF 1	1,500	0.97	1.7
SF 2	13,000	0.98	1.8

[1] from SEC using polystyrene standards
[2] from elemental analysis and titration of unreacted acid groups.

ω-C_6F_{13} polymethylmethacrylate was also synthesized by radical telomerization using methylmethacrylate as a taxogen, $n.C_6F_{13}$-C_2H_4-SH as a telogen and azobisisobutyronitrile (AIBN) as an initiator in acetonitrile (AN) at 60°C for 10 hours (5).

$$n\ CH_2\!=\!\overset{\displaystyle CH_3}{\underset{\displaystyle COOCH_3}{\overset{\displaystyle |}{\underset{\displaystyle |}{C}}}}\quad +\ HS\text{-}C_2H_4\text{-}C_6F_{13}\quad \xrightarrow[\text{60°C, 10 h}]{\text{A.I.B.N. (AN)}}$$

$$H\!-\!\!\left[\!CH_2\text{-}\overset{\displaystyle CH_3}{\underset{\displaystyle COOCH_3}{\overset{\displaystyle |}{\underset{\displaystyle |}{C}}}}\!\!\right]_{\!n}\!\!-\!S\text{-}C_2H_4\text{-}C_6F_{13}\qquad\qquad (6)$$

The final polymer was precipitated in heptane, filtered and dried under vacuum. It was characterized by SEC, IR, ^{19}F NMR, and elemental analysis (Table III).

TABLE III.

Molecular characteristics of ω-C_6F_{13} PMMA samples.

Sample	$\overline{M}_n$ [1]	Functionality [2]	$\overline{M}_w/\overline{M}_n$
MF 1	1,500	0.99	1.6
MF 2	4,400	1.00	1.5

[1] from SEC using polystyrene standards
[2] from elemental analysis and $\overline{M}_n$.

Styrene and MMA were dried overnight over calcium hydride and distilled under vacuum. Styrene was finally distilled from fluorenyllithium just before use. D_3 was dried overnight over calcium hydride and sublimated under vacuum; it was then sublimated from n.Butyllithium just before use. Toluene was dried by refluxing over calcium hydride and THF was dried by refluxing over a sodium/benzophenone complex; THF was also distilled from polystyryllithium oligomers just before use. The other solvents and reagents were used as received.

Surface characterization

Surface tension of two-component polymer additives solutions. Surface tension of additive solutions in THF or CCl_4 was measured by the Wilhelmy plate method (6) with a Krüss K10 Digital Tensiometer at 25°C.

Wettability of polymer films. Surface tension of PS films added with various amounts of P(S-b-DMS) was measured as follows. When a liquid is spread out on a solid surface of a lower surface tension, it tends to re-form the original drop. Would the surface energy of the liquid be equal to or lower than that of the solid and the liquid tends to form a film on the solid surface. Thus using a series of chemically inert liquid-liquid mixtures covering a large domain of surface tensions, it is possible to straddle the actual surface tension of the surface by the visual observation of its wettability. Ethanol-water mixtures, the surface tension of which varies from 22 to 36 mN/m at 25°C, were purposely used (7).

Contact angle measurements (8). Contact angles of water droplets (vol. $5\,\mu l$) on PS films containing various amounts of ω-C_6F_{13} PS were measured at 25°C by the sessile drop method. A home-made apparatus consisted of a halogen lamp, a sample holder and a telelens allowing a magnified drop picture to be observed on a screen and the contact angle to be measured accurately.

XPS (9). Photoelectron spectra were recorded using a Hewlet-Packard 5950 A ESCA spectrometer equipped with a monochromatized Al $K\alpha$ X-ray source (hν = 1486.6 eV). The analysis chamber was kept at 300 K under a pressure in the 10^{-7} Pa range. Spectra were recorded with the "electron flood gun technique" to neutralize spurious charging effects. XPS peak intensity was normalized and used to calculate the relative

abundance of elements (Si/C and F/C) at the film surface. Measured peak area was divided by a relative strength factor which was determined from the elemental ratios of standard compounds, i.e. C_{1s} = 1.00, Si_{2p} = 0.90 and F_{1s} = 4.08 (10).

Film formation. Films were prepared by casting 5.0 wt % solutions of polymer plus additive in THF or CCl_4. The substrate was a clean glass slide for wettability and contact angle measurements and a stainless steel holder for XPS measurements. Solvent was slowly evaporated at room temperature under normal pressure. Films were further dried under vacuum for 48 hours before use. Films of PS modified by P(S-b-DMS) were carefully peeled from the glass slide in order to measure wettability on both sides : polymer/air and polymer/glass, respectively.

RESULTS AND DISCUSSION
Surface tension of copolymer solutions

In a preliminary step, the two-component additives have been dissolved in THF or CCl_4 in order to check their potential activity at an air/liquid interface. Whatever the additive (diblock copolymer or fluorine ended homopolymer), the dependence of the surface tension (γ) on additive concentration is very similar. A fast initial decrease in surface tension is followed by the levelling off of that parameter (FIGS. 1 and 2). The concentration at which the slope changes dramatically is generally attributed to the critical micellar concentration (c.m.c.), at least for surfactant solutions (11,12). Figures 1 and 2 show that c.m.c. of 0.5 wt % solutions of P(S-b-DMS) in THF is mainly independent of molecular weight and composition of the diblock
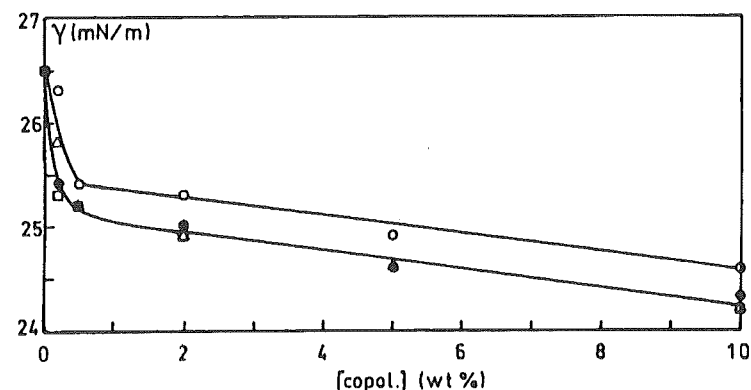
FIG. 1.

Surface tension of P(S-b-DMS) solutions in THF in relation to copolymer concentration : influence of molecular weight at constant copolymer composition. Copolymer S1 (o); copolymer S2 (Δ); copolymer S3 (●); copolymer S4 ($\square$).

copolymers. When solution surface tensions are compared in the "plateau" region, it is clear that, at a constant copolymer composition of 40 wt % PDMS, γ decreases as the molecular weight increases up to 19,000. Beyond that molecular weight, γ does not change anymore (FIG. 1). Figure 2 allows us to compare diblock copolymers containing the same PS block ($\overline{M}_n$: 12,000). γ is largely insensitive to the diblock composition from 8 to 19 wt % PDMS. A jump to higher γ values obviously occurs between 19 and 35 wt %, whereas the surface tension remains unchanged up to 64 wt % PDMS. A sigmoid-like dependence of γ vs. copolymer composition might thus be suggested in a composition range from 8 to 64 wt % PDMS. It must however be pointed out that the effects reported in Figures 1 and 2 are very small and this might be attributed to the solvent, which is a good solvent for both PS and PDMS blocks. The availability of a selective solvent of PS (or PDMS) is quite a problem.
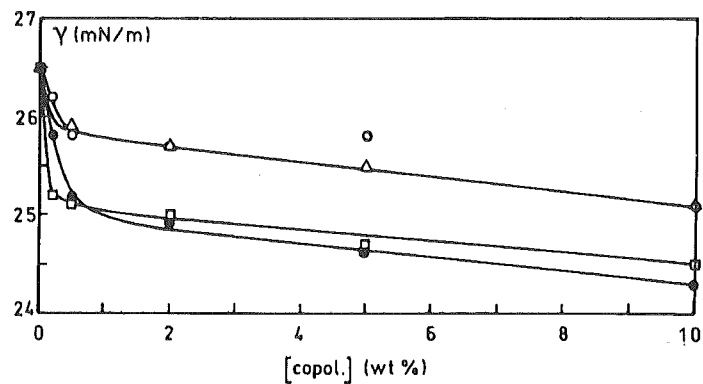
FIG. 2.

Surface tension of P(S-b-DMS) solutions in THF in relation to copolymer concentration : influence of copolymer composition at constant PS block. Copolymer S5 (o); copolymer S6 (Δ); copolymer S2 (●); copolymer S7 (□).

Compared to P(S-b-DMS), plots of γ vs. concentration characteristic of ω-C_6F_{13} PS and PMMA display a sharp change in the slope at a much higher concentration (at least 10 fold higher). In THF - a common solvent of the two components of the additives - the surface activity of ω-C_6F_{13} PS is slightly higher than that of ω-C_6F_{13} PMMA (FIG. 3). Furthermore, the effect of the molecular weight of PS and PMMA on γ is again very small within the limits of the investigated range. Interestingly enough, in CCl_4 which is a selective solvent of the polymeric backbone, the surface activity of the additive has dramatically increased compared to THF solutions. The experimental γ value (ca : 21 mN/m) is indeed intermediate to 17.0 and 22.5 mN/m which are the reported values for a CF_3- and -CF_2- fully covered surface, respectively (13). This behaviour reflects the preferential location of the fluorinated segment of the additive at the liquid surface. It also illustrates how dramatic the thermodynamic quality of the solvent towards each component of the additive is, as far as the control of the surface tension of that liquid is concerned.
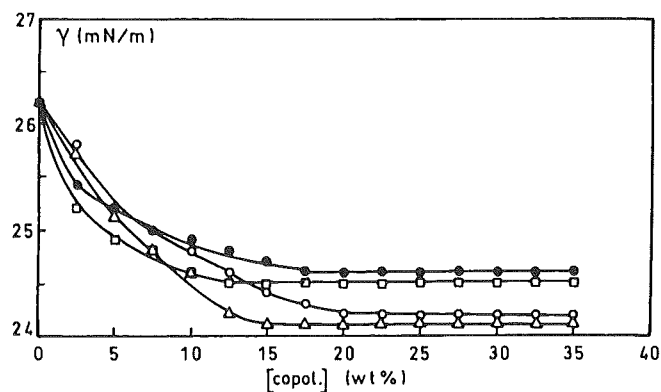

FIG. 3.

Surface tension of ω-C_6F_{13} PS and PMMA solutions in THF in relation to copolymer concentration. Copolymer SF2 (o); polymer SF1 (Δ); polymer MF1 (●); polymer MF2 (□).
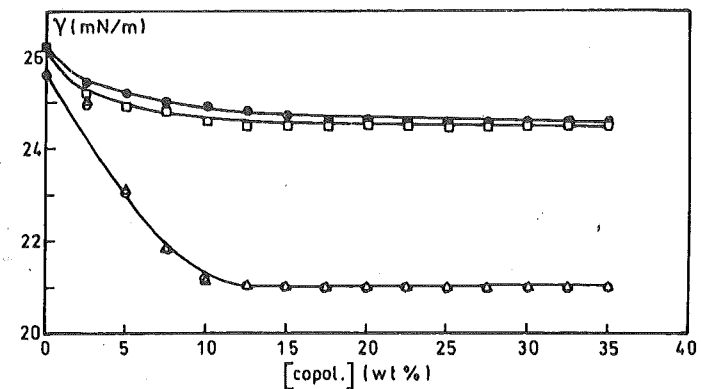

FIG. 4.

Surface tension of ω-C_6F_{13} PMMA solutions in relation to polymer concentration : influence of solvent. Polymer MF1 in THF (●); polymer MF2 in THF (□); polymer MF1 in CCl_4 (o); polymer MF2 in CCl_4 (Δ).

Analysis of polymer films

Surface tension of PS films modified by various amounts of P(S-b-DMS) has been estimated by the wettability technique using a series of liquids of a well-known surface tension. Seemingly, 0.5 wt % of a diblock is enough to decrease γ of polystyrene to the value characteristic of the PDMS segment (FIG. 5) (14,15). A unique curve has actually been recorded for a series of 4 diblocks of different length and composition. The experimental surface tension is also the same on both the air/polymer and glass/polymer sides. In contrast to THF, the PS matrix is a selective non-solvent of the PDMS block. It is worth noting that the c.m.c. of the diblock remains as small in the PS matrix as in THF, although its surface activity is basically different (FIG. 1 and 5). This emphasizes again the critical importance of the mutual interactions of each component of the additive with the continuous phase on the surface energy of that phase.
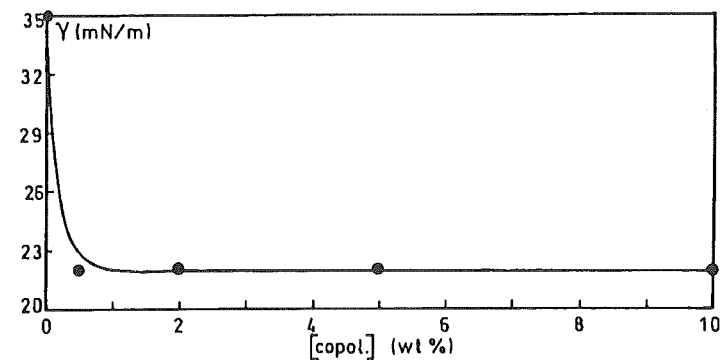

FIG. 5.

Surface tension of PS films modified by P(S-b-DMS) in relation to copolymer concentration (wettability measurements). Copolymer S1 (●); copolymer S2 (●); copolymer S3 (●); copolymer S4 (●).

The surface of some of the previous films has been analyzed by XPS (FIG. 6). The experimental data are very consistent with wettability measurements since the surface Si content increases rapidly with the diblock amount and tends to a maximum value beyond ca. 0.5 wt %. The surface Si/C atomic ratio (0.15-0.20) is then intermediate to the theoretical values for pure PDMS (0.5) and pure PS (0.0). XPS provides not only a more quantitative information than wettability but it also allows to evidence an effect of the molecular weight of the diblock (of a constant composition) on the surface activity (FIG. 6).
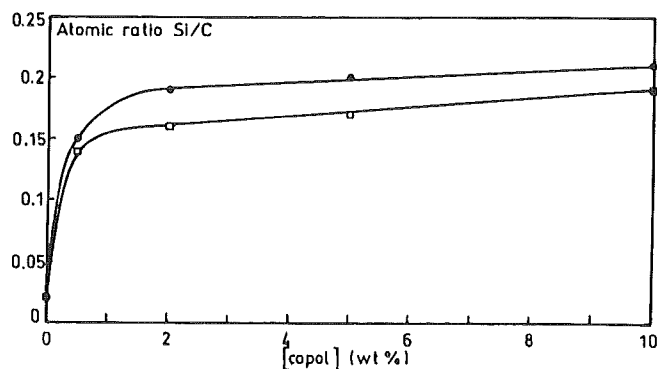
FIG. 6.

Surface Si/C atomic ratio of PS films modified by P(S-b-DMS) in relation to copolymer concentration : influence of molecular weight at constant copolymer composition. Copolymer S1 (●); copolymer S2 (□).

The solvent used for the film casting has no decisive effect on the surface tension of polystyrene ω-C_6F_{13} PS of two different molecular weights have been dissolved in THF and CCl_4, respectively. Figure 7 shows that γ is independent of the relative thermodynamic quality of the solvent towards PS and the -C_6F_{13}
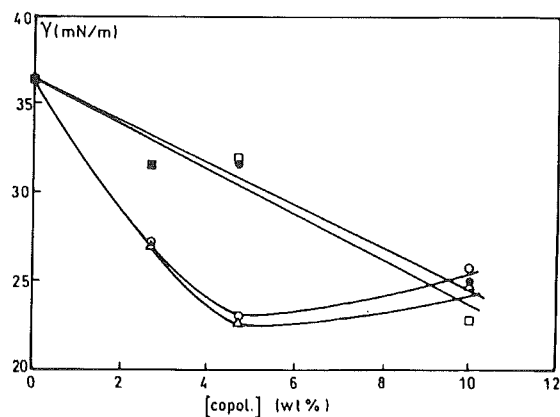
FIG. 7.

Surface tension of PS films modified by various amounts of ω-C_6F_{13} PS : influence of the additive molecular weight. Surface tensions were calculated from contact angle measurements. Additive SF2, film cast from THF (o); additive SF2, film cast from CCl4 (Δ); additive SF1, film cast from THF (●); additive SF1, film cast from CCl_4 (□).

end-group. Clearly, the molecular weight of ω-C_6F_{13} PS has a very significant effect on the surface tension of PS. This behaviour is illustrated in a consistent manner by contact angle measurements (FIG. 7) and XPS data (FIG. 8). At low additive concentrations, the longest chains are more effective in changing the PS surface and a c.m.c. close to 4 wt % is observed. The low molecular weight additive affects the PS surface in a rather continuous way as shown by the approximately linear dependence of surface tension (FIG. 7) and surface fluorine content (FIG. 8) on the additive percentage. No c.m.c. can be detected below an additive content of 10 wt %.
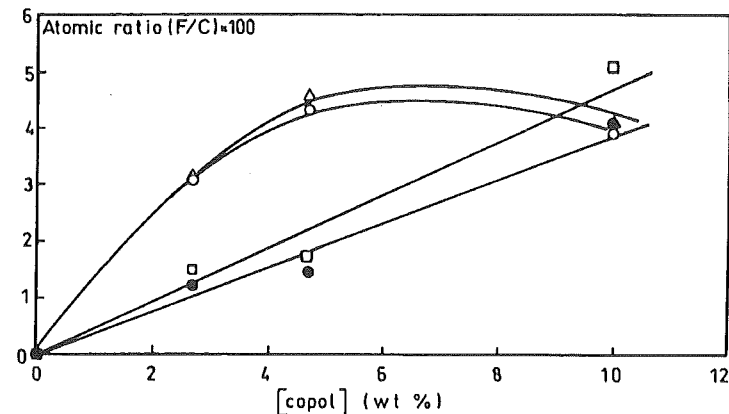
FIG. 8.

Surface F/C atomic ratio of PS films modified by various amounts of ω-C_6F_{13} PS : influence of additive molecular weight. Additive SF2, film cast from THF (o); additive SF2, film cast from CCl4 (Δ), additive SF1, film cast from THF (●), additive SF1, film cast from CCl_4 (□).

Figures 5 and 7 provide an interesting information on the relative efficiency of P(S-b-DMS) and ω-C_6F_{13} PS in decreasing the PS surface tension. When these two additives comprise the same PS component ($\overline{M}_n$: 12-13,000) and are used at the same concentration (4 wt %), they have the same surface activity. Let us note that the component of the low surface energy is very short in the fluorinated material (molecular weight C_6F_{13} : 319) compared to the PDMS block ($\overline{M}_n$: 6,500). As a consequence, the molar amount of ω-C_6F_{13} is higher than that of the P(S-b-DMS) copolymer. On the basis of the experimental c.m.c. values, the use of the diblock copolymer is more attractive than that of the C_6F_{13} end-capped polystyrene.

CONCLUSION

Surface tension of organic solvents and, more interestingly, surface energy of a polymeric matrix (e.g. polystyrene) can be significantly reduced by very small amounts of either a polydimethylsiloxane containing diblock copolymer or a polymeric backbone end-capped with a fluorinated moiety (C_6F_{13}). The component of the low surface energy must be associated to a polymeric partner selectively soluble in the organic solvent or miscible (or identical) to the polymeric matrix. Relative interactions of the dispersion medium with each component of the additive are indeed of a prime importance in the control of the surface energy. Within these limits, there is an obvious similarity in the colloidal behaviour of the additive whatever the dispersion medium : organic solvent or polymeric matrix.

ACKNOWLEDGMENT

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ON THE TAUTOMERIC STRUCTURE OF 5-HYDROXY- AND 5-MERCAPTO-1H-1,2,3-TRIAZOLES : ^{13}C NMR ANALYSIS

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Dedicated to Professor G. Smets on the occasion of his 75th birthday

The title compounds have been analyzed by ^{13}C NMR spectroscopy and compared with the N-3 methyl and O/S alkyl derivatives. The mesoionic structures **2a,b** are rejected in favour of **1a,b** on the basis of the $^{2}J_{C5=CH}$ coupling constants and the chemical shifts. Incremental substituent effects for triazoles are discussed.

5-Hydroxy-[1-6] and 5-mercapto-1H-1,2,3-triazoles[7-10] have been prepared on several occasions and are usually drawn as the aromatic structures **1a,b**, although the mesoionic structures **2a,b** are also conceivable.

a: X=O;   b: X=S
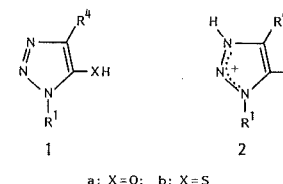
Tautomeric structures with the mobile hydrogen at the positions N-2 and C-4 are easily discarded by spectroscopic analysis, but a distinction between **1** and **2** is less straightforward. Most authors favour the aromatic structures **1a,b** on the basis of IR data, while others[10] propose the mesoionic structure **2b** from their UV analysis. Furthermore, structure **2** deserves strong consideration in view of the fact that triazoles are alkylated at the N-3 position.[11]

Consequently, we have analyzed the ^{13}C NMR spectra of the C-4 unsubstituted parent compounds **3** and **6**, and compared the results with those from the N-3 methylated[12] and O/S alkylated derivatives;[13] the results are summarized in Scheme I.

The most convincing evidence for structures **3** and **6** is the two-bond coupling constant between C-5 and H-4, whose value ($^{2}J_{C=CH}$ = 14 Hz) is diagnostic for 5-substituted triazoles[14] and different from that of the mesoionic structures **4** and **7** (~ 11 Hz).[12]

The chemical shifts of the triazole C-atoms also favour our structure assignment. Indeed, compared with 1-phenyl-1,2,3-triazole (C-4 at δ 134.1, C-5 at δ 121.5)[15] the OH group in **3** exercises a downfield shift of 30.7 ppm on C-5 and an upfield shift of 18 ppm on C-4,[16] while the SH group in **6** shifts both C-4 and C-5 downfield by 2.8-2.9 ppm. These substituent effects are similar to those observed in benzene.[17]