# NMR and SANS Study of Poly(methyl methacrylate)-*block*-poly(acrylic acid) Micelles and Their Solubilization Interactions with Organic Solubilizates in $D_2O$

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ABSTRACT: Poly(methyl methacrylate)-*block*-poly(acrylic acid) copolymers (PMMA−PAAc) neutralized to various degrees with Li, Na, or K counterions were synthesized and their micellar solutions in $D_2O$ were studied using $^1H$ and $^7Li$ NMR and SANS. The micelles solubilize organic substances such as chloroform or chlorobenzene under swelling of their PMMA cores with a kinetics controlled mainly by the interaction parameter between the solubilizate and PMMA. The solubilizate is shown to be mainly distributed in the inner area of the micellar corona in the early stages of the solubilization process, later both in the micellar core and along the chains of the corona, in particular in the case of PMMA−PAAc micelles in their acid form. By neutralizing the PAAc chains to various degrees and observing both the NMR spectra and the longitudinal relaxation rate of $^1H$ and $^7Li$, changes of conformation and mobility of the PAAc chains can be deduced. With increasing neutralization degree, the solubilization is accelerated but the equilibrium degree of solubilization is slightly lower. The solubilizate transport between PMMA−PAAc and polystyrene-*block*-poly(methacrylic acid) (PS−PMAc) in their sodium forms is demonstrated, showing solubilization selectivity.

## Introduction

The tendency of amphiphilic block copolymers consisting of one hydrophobic block such as polystyrene or poly(methyl methacrylate) and one hydrophilic block such as poly(methacrylic acid) or its alkaline salts to form micelles of a remarkably uniform size distribution in water has been known for some time.[1,2] The ability of such micelles to solubilize various hydrophobic organic molecules was demonstrated by various techniques such as gas chromatography, fluorescence, and light scattering.[3−6] Most of the methods just mentioned give information about some aspects of the system's behavior, and accordingly, any independent method can be valuable for its deeper understanding. The potentialities of NMR have been utilized in a few studies of block copolymer micellization in organic solvents,[7−10] but almost no work appears to have been done on aqueous systems and solubilizations. Our first results in this field are presented here. As our main object, since poly(methyl methacrylate)-*block*-poly(acrylic acid) and its alkaline salts have not been studied so far, we include some additional results obtained with light and neutron scattering.

## Experimental Section

**Chemicals.** Poly(methyl methacrylate)-*block*-poly(acrylic acid) (PMMA−PAAc) was prepared in the following way: poly(methyl methacrylate)-*block*-poly(*tert*-butyl acrylate) of varying relative and absolute lengths of the polymer blocks was prepared by group-transfer polymerization and characterized using methods published earlier.[11−13] The copolymer on which most of the experiments reported here were performed had the average $M_n = 20\,000$, $M_w/M_n = 1.8$ and average polymerization degrees of MMA and PAAc blocks of 93 and 149, respectively. Selective acidolysis of the polyacrylate blocks to PAAc under cleavage of isobutylene was done using *p*-toluenesulfonic acid as a catalyst.[14] A fraction of the *tert*-butyl groups of about 3 mol % was left unhydrolyzed as a valuable indicator of the PAAc-chains behavior. The catalyst and other low-molecular-weight impurities were removed by dialysis with water, and the aqueous polymer solution was then lyophilized.

Poly(styrene)-*block*-poly(methacrylic acid) copolymers (PS−PMAc) were prepared by anionic block copolymerization of styrene with methyl methacrylate and subsequent hydrolysis of the PMMA block in HCl−dioxane mixture.[15]

Micelles of the PMMA−PAAc copolymer with PMMA cores were prepared by direct dissolution in a water−dioxane mixture and then transferred into dioxane-free $D_2O$ media by a stepwise dialysis.[1,2]

**Nuclear Magnetic Resonance (NMR) Measurements.** $^1H$ NMR spectra and relaxations were measured at 300.1 MHz with a Bruker ACF 300 spectrometer under presaturation of the residual signal of $H_2O$ and using an external standard. $^7Li$ NMR spectra were measured at 77.7 MHz with a Varian Unity 200 spectrometer.

**Small-Angle Neutron Scattering (SANS) Measurements.** SANS measurements were performed using the time-of-flight small-angle neutron spectrometer YuMO using a chopped neutron beam at the IBR-2 pulse reactor in the Joint Institute for Nuclear Research, Dubna.[16] The solution of concentration 3.65 mg/mL was placed at the temperature 20 °C in an optical quartz cell with a path length of 2 mm. All measurements were corrected for background scattering and normalized using a vanadium standard.[17]

The experimental SANS curves were fitted by a scattering curve for homogeneous spherical particles with a two-parameter Schulz−Zimm distribution of radii.[18] In this case, the theoretical fitting function was

$$P(q) = \int_0^\infty F(q,R)^2 f_z(R)\, \mathrm{d}R$$

where the form factor for a sphere of radius $R$ and scattering contrast $\Delta\rho$ is

$$F(q,R) = \frac{4}{3}\pi R^3 \Delta\rho \Phi(qR)$$

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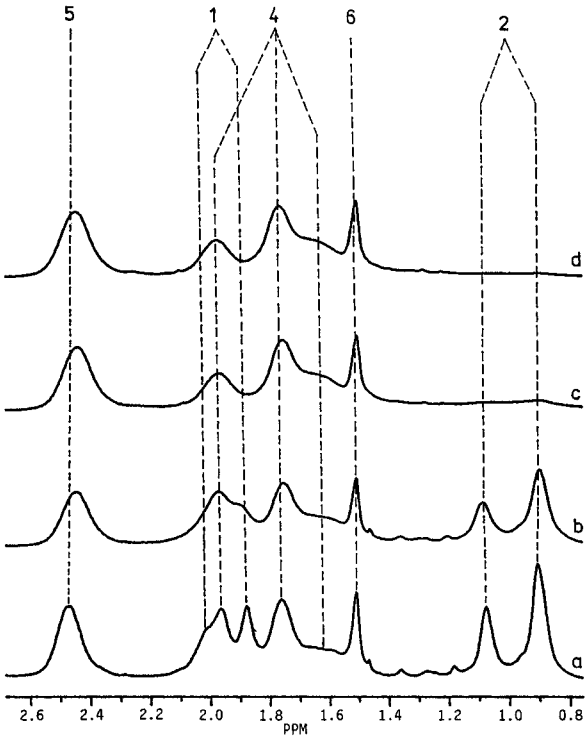



**Figure 1.** Parts of the 300 MHz $^1$H NMR spectra of the 2% w/w dioxane solutions of PMMA−PAAc after the addition of (a) 0, (b) 40, (c) 80, and (d) 120% w/w of $D_2O$. Signals of protons 3 are obscured by the signal of the solvent and are not shown.

$$\Phi(qR) = 3\frac{\sin(qR) - qR\cos(qR)}{(qR)^3}$$

The Schulz−Zimm distribution is a two-parameter function:

$$f_z(R) = \left(\frac{Z+1}{R_m}\right)^{z+1}\frac{R^2}{\Gamma(Z+1)}\exp\left\{-\left(\frac{Z+1}{R_m}\right)R\right\}$$

where $R_m$ is the mean radius, $Z$ is a width parameter ($Z > -1$), and $\Gamma(x)$ is the gamma function.

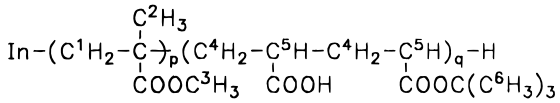
The initial part of the SANS curves ($q < 0.2$ Å$^{-1}$), which can be affected by the scattering from micellar corona and by the interparticle interference, was not taken into account. Thus, the fit provides the parameters related to the micellar cores.

## Results and Discussion

Figure 1a shows the relevant part of the $^1$H NMR spectrum of the 0.5% w/w poly(methyl methacrylate)-*block*-poly(acrylic acid) (PMMA−PAAc) solution in dioxane at 298 K except the region of the O−$CH_3$ protons which is obscured by the signal of the solvent. The signals are numbered according to Chart 1.

Here, $p$ and $q$ are the main polymerization degrees of the blocks and In means the initiating group. The minority *tert*-butyl groups are dispersed randomly along the PAAc chain in the concentration 3 mol % relative to all its carboxylic groups. Since the copolymer is soluble molecularly in dioxane, all PMMA as well as PAAc signals can be observed with shapes analogous to those of the corresponding homopolymer solutions. If water or $D_2O$ is added to the dioxane solution (amount of $D_2O$ added to the system increases in Figure 1 from 0 to 120% w/w), the PMMA blocks become insoluble and associate, thus forming micelles. In the association process, PMMA chains clearly decrease their mobility, as can be observed in a broadening of the corresponding NMR signals, and finally reach a quasi-glassy state in

**Chart 1**




which their signals are broadened beyond detection with a high-resolution NMR. The same block copolymer is directly soluble in water or $D_2O$ and forms micelles at the concentration 0.5% w/w or less. SANS experiments show that the micelles comprise about 200 macromolecules and the mean radius of their cores is 7.9 nm. Along with the micellar form, unimer is always present in a small fraction from 3 to 8 mol % (relatively to all copolymer molecules) depending on temperature and neutralization degree of the PAAc chains. This can be seen in Figures 2 and 3 where the spectrum of the purely acid form of a 0.5% solution of the copolymer in $D_2O$ is compared with those with 20, 40, 60, 80, and 100% neutralization with LiOH (Figure 2) and NaOH (Figure 3). The signals of the protons marked as 1, 2, and 3 of the unimer are observable (and distinguished as 1U and 3U in Figures 2 and 3) due to their mobility, which is much larger in the dissolved state. Owing to this, the number of the macromolecules associated in an average micelle can be alternately measured by NMR. Assuming a true equilibrium between $n$ unimers U and a micelle M, an average value of $n$ can be obtained from the linear relation

$$\log[(1-\varphi)c] = n\log(\varphi c) + \log(Kn) \qquad (1)$$

where $\varphi$ is the molar fraction of unimer macromolecules and $c$ is the molar concentration of the copolymer taken without respect to its association. Assuming the full detectability of all proton signals of the unimer but only those of the PAAc chains in the copolymers associated in a micelle, the molar fraction $\varphi$ can be obtained from the relation

$$\varphi = (q/p)(I_r/I_u - 5/3)^{-1} \qquad (2)$$

where $p$ and $q$ are the mean polymerization degrees of the blocks as defined in Chart 1, the integral signal intensity $I_u$ corresponds to the unimer signal 3 and $I_r$ is that of the residual spectrum. If some part of the unimer molecule is invisible in NMR, which could happen due to intramolecular association, relation 2 is wrong by some factor which, however, should not depend markedly on concentration so that relation 1 with the apparent $\varphi$ should still be linear but shifted by some factor. The concentration span attainable for NMR investigating relation 1 is rather narrow, from 0.1 to 0.5% w/w, the upper boundary being given by possible further association of the micelles at higher concentrations, which can be observed, e.g., by light scattering, and the lower one by sensitivity. In Figure 4, there are given the dependences of the apparent value of $\varphi$ of the fully neutralized sodium salt of the copolymer on its molar concentration in (a) pure $D_2O$ and (b) in 0.05 mol/L NaCl solution in $D_2O$. No sensible dependence corresponding to relation 1 can be obtained from either of these curves which indicates that no simple equilibrium exists between the unimers and the micelles in spite of the uniform distribution of the latter.

Considering these results, one has to bear in mind that the polymer block in the core is in a quasi-glassy state; i.e. the micelle is a nonequilibrium system for which the usual concepts such as the critical micellar

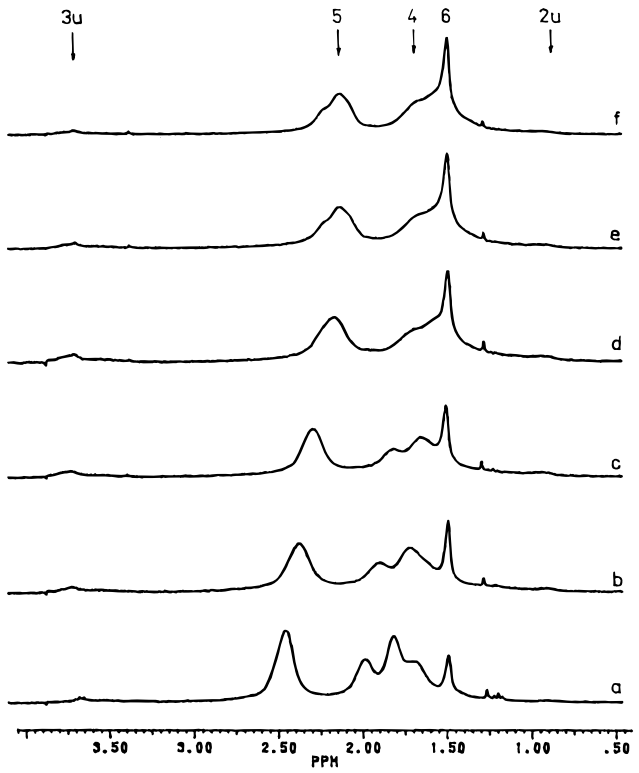



**Figure 2.** 1H NMR spectra of 0.5% w/w $D_2O$ solutions of PMMA−PAAc neutralized to (a) 0, (b) 20, (c) 40, (d) 60, (e) 80, and (f) 100% with LiOH.

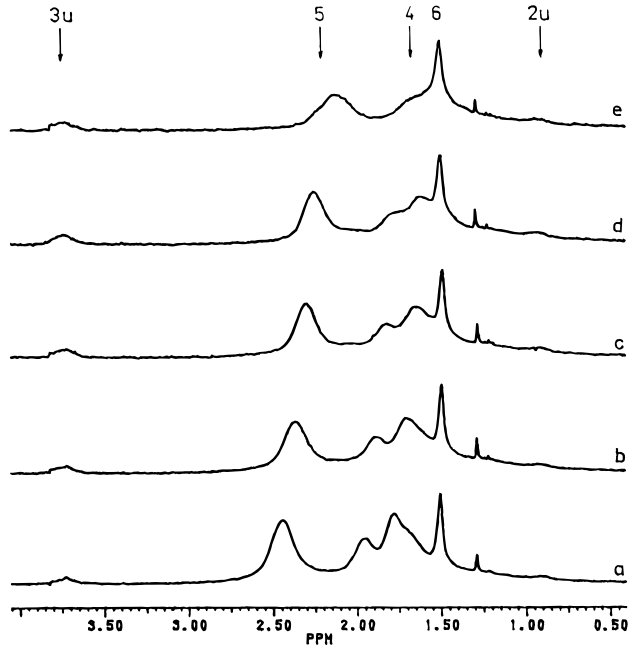



**Figure 3.** 1H NMR spectra of 0.5% w/w $D_2O$ solutions of PMMA−PAAc neutralized to (a) 20, (b) 40, (c) 60, (d) 80, and (e) 100 % with NaOH.

concentration have no clear meaning. Ideally, no unimer molecules should be produced if all the core chains were in a similarly immobilized state. Our results show that some of them are less anchored in the core and are thus able to escape from the micelle more easily than the others. The difference between both dependences indicates that this effect is largely suppressed but not entirely excluded by increasing ionic strength.

In Figures 2 and 3, the PAAc part of the NMR spectrum changes with increasing neutralization degree in both the chemical shift and the width of the signals

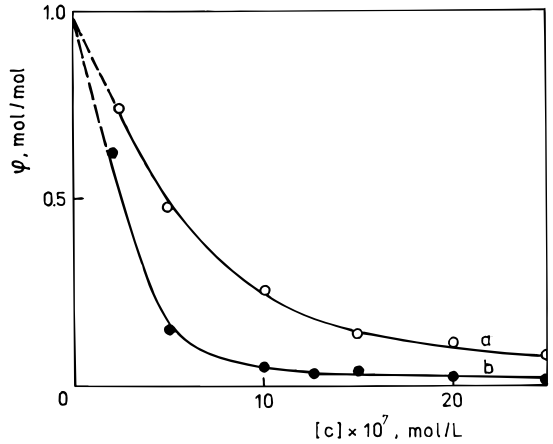



**Figure 4.** Dependence of the apparent unimer molar fraction $\varphi$ on the molar concentration $c$ of PMMA−PAANa in $D_2O$ (○) and in a 0.05 mol/L solution of NaCl in $D_2O$ (●).

of protons marked as 4 and 5. The signals of protons 5 shift not only collectively but also relatively so that the two originally nonequivalent $CH_2$ protons of the isotactic dyad attain near-equivalence. At the same time, the signal of protons 6 becomes superimposed on that of proton 5 so that it seemingly increases its intensity. Deconvolution of the signals using the program GLINFIT shows signal 6 to remain constant in shift and intensity but somewhat broadened in highly neutralized samples. It should also be noted that resonance 6 splits, producing another rather sharp weak signal upfield from the original one. This resonance can be observed, sometimes with a much higher intensity, in cases where interactions of the micelles with organic solubilizates occur and has to be interpreted as a sign of a changed conformation of the PAAc chain.

As the width of the signals is largest in the case of the fully neutralized PAAc, the signal broadening cannot be due to chemical exchange between acid and neutralized groups only and should be, partly at least, a consequence of the gradual chain stiffening due to electrostatic repulsions between the carboxylic anions. This problem can be addressed by a relaxation study which is underway in our laboratory.

Figure 5 shows the SANS curves of the micellar solutions at various degrees of neutralization. One can see that the SANS curve of the acid form is very different from those of neutralized ones. The data analysis reveals that the volume of the micellar core in the former case appears to be 40% larger than for partly or fully neutralized PAAc (see also Figure 8). This finding is complemented by the fact that solubilization of a good solvent such as chloroform by the acid form leads, among other changes, to a 21% increase in the absolute intensity of the NMR signal of the protons marked as 4. The only plausible explanation of the findings appears to be that a corresponding part of the PAAc chains is attached to the micellar core, possibly tightly folded or entangled in its vicinity, and thus relatively immobilized in the acid form.

Perhaps even more interesting is the narrowing and thus emerging of the NMR signals of the PMMA part in the course of the micellar core swelling by a good solvent. The ability of the solvent to narrow the signals of the core depends on the resulting segmental mobility of the swollen core-forming blocks which depends on both the amount of the solubilized solvent and its ability to interfere with the inter- or intra-chain interactions. Therefore, both the solvent power expressed, e.g., by the

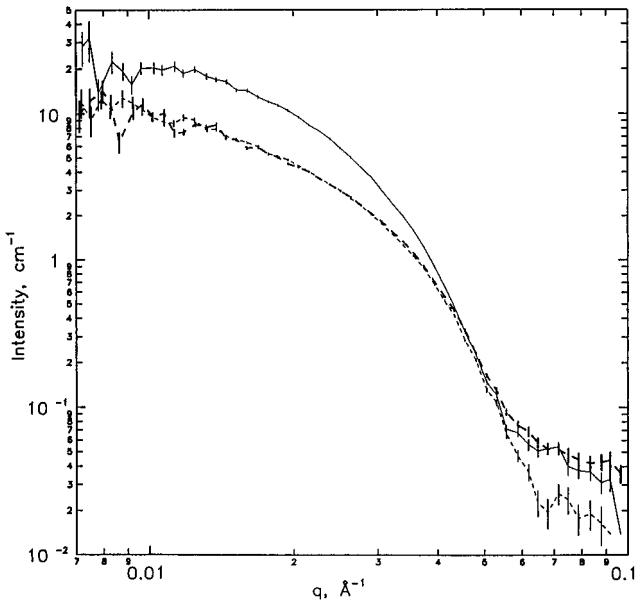



**Figure 5.** Experimental SANS curves (points with error bars) for the PMMA−PAAc micelles neutralized with LiOH. Degree of neutralization in % mol: 0 (full line), 20 (dashed line), and 100 (dotted line).

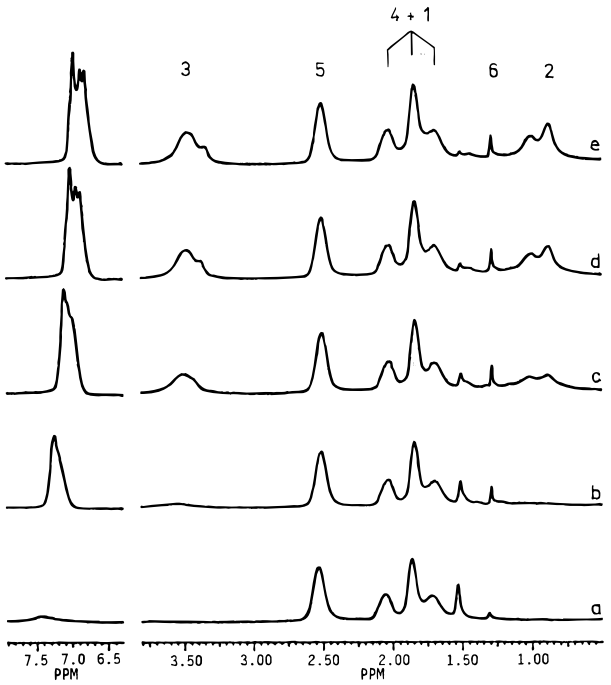



**Figure 6.** 1H NMR spectra of the 0.5% w/w $D_2O$ solution of PMMA−PAAc with overlayed chlorobenzene after (a) 20, (b) 160, (c) 300, (d) 440, and (e) 580 min.

value of the Huggins $\chi$ parameter, and temperature influence this phenomenon. Thus, e.g., chlorobenzene appears to be quite inactive to PMMA−PAAc micellar solution at room temperature but, at 350 K, its effect is similar to that of chloroform. This is demonstrated in Figure 6, showing the effect of increasing solubilization in the 0.5% micellar solution of PMMA−PAAc in $D_2O$ overlayed with chlorobenzene. Figure 7 shows the same for PMMA−PAALi, i.e. the PAAc block fully neutralized with LiOH. These figures show the convenience and information content of the solubilization kinetics measurement when using NMR. The amount of the solubilizate measured by the absolute integral intensity of its signal is about the same in both forms of the polymer at the equilibrium but the solubilization is somewhat

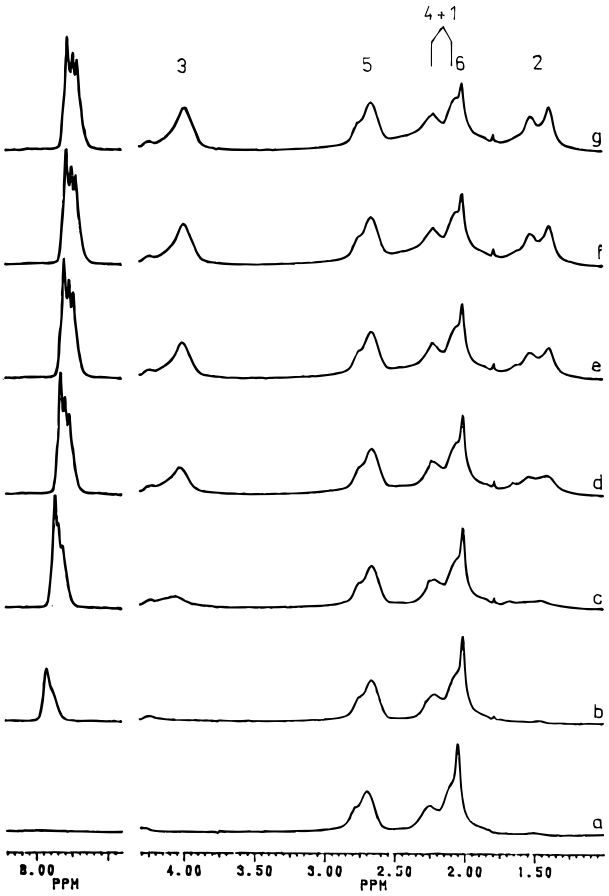



**Figure 7.** 1H NMR spectra of the 0.5% w/w $D_2O$ solution of PMMA−PAALi with overlayed chlorobenzene after (a) 7, (b) 134, (c) 261, (d) 380, (e) 515, (f) 642, and (g) 769 min.

faster in the case of the Li form. The small difference between both cases suggests that the solubilization rate is chiefly controlled by the diffusion of the solubilizate into water and through it. In addition, several interesting features are revealed in these spectra. The signal of the solubilizate shifts in the early stages and gradually splits into three components. At the same time, the growing signal of the pendant O−$CH_3$ group splits into two components and that of the *tert*-butyl groups randomly scattered on the corona chains initially splits into two components and then broadens and splits further. These changes can be observed with both acid and neutralized forms of the corona but are more apparent in the former case. The skeletal, i.e. methine and methylene, signals of the corona chains appear to be unaffected. These features can be interpreted, we believe, in the following way. The solubilizate (chlorobenzene in this case, but chloroform as well): (a) is distributed mainly in the micellar core but partly in the corona as well and (b) forms a weak molecular complex with the ester groups of PMMA in the core and with the carboxylic groups of PAAc in the corona, in particular in its acid form. Both phenomena are not necessarily connected: from the initial upfield shift of the solubilizate signal at the stage where almost no core signals emerge one could deduce that a substantial part of the solubilizate resides in the inner part of the corona before and even after its entering the core. However, mere traces of the split *tert*-butyl signal can be observed at the initial stage, which suggests that the reorganization process proceeds in the corona simultaneously with the core swelling. Analogous effects appear with other solvents with the proviso that acid forms of PMMA−

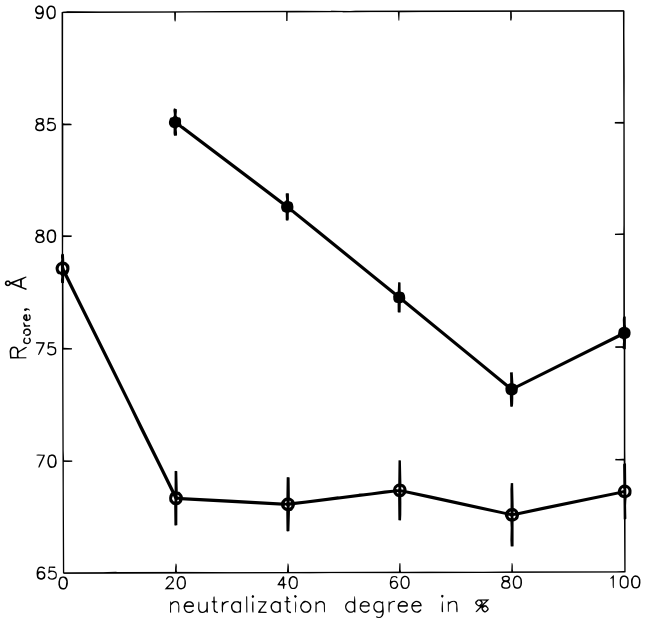



**Figure 8.** Dependence of the mean radius of the micellar core on the neutralization degree of the PMMA−PAAc micelles before (○) and after (●) chloroform solubilization.

PAAc with aromatic solubilizates were the typical cases where substantial splittings of the said signals can be observed.

Parallel to the NMR measurements, a SANS study of chloroform solubilization by PMMA−PAAc neutralized with LiOH was done. A more detailed description of the interpretation procedures and complete results for the solubilization phenomenon will be given in a separate publication. For the purpose of this study only the variations of the micellar radius with the degree of neutralization are shown in Figure 8. Whereas the core radius in the absence of solubilizate appears to be only slightly dependent on the neutralization degree except for the purely acid form of the micelle, in the equilibrium systems with chloroform there is a gradual decrease in the swollen core radius with the increasing neutralization degree. Again, this phenomenon is far from being simple but can be explained by a partial adhesion of the inner part of the corona chains to the core. This conjecture is corroborated by our NMR observation that the absolute intensity of the proton 5 signals of the corona PAA chain increased, along with the signals of the core PMMA, by about 15% of its original magnitude.

Finally, the ability of NMR to observe intermicellar exchange of the solubilizate is demonstrated in Figure 9. Here, (a) the fully neutralized Na form of PMMA−PAAc in 0.5% micellar solution in $D_2O$ lacks signals of PMMA except those belonging to a small fraction of the unimer present but (b), after equilibrium mixing with chloroform and phase separation, exhibits nicely developed signals of the protons marked as 3 and partly 4; (c) the Na form of PS−PMAc at the same concentration shows no polystyrene signals as expected but (d) reveals them in the equilibrium system after treatment with chloroform. If system b is mixed with a 2-fold excess of (c), part of the chloroform solubilized in PMMA−PAAc is transferred into the core of PS−PMAc, revealing thus a part of the PS signals and lowering the intensity of those of PMMA, as shown in (e). If, however, (d) is mixed with an analogous excess of (a), all PS signals disappear and PMMA signals emerge, as shown in (f). This shows a greater affinity of chloroform to the

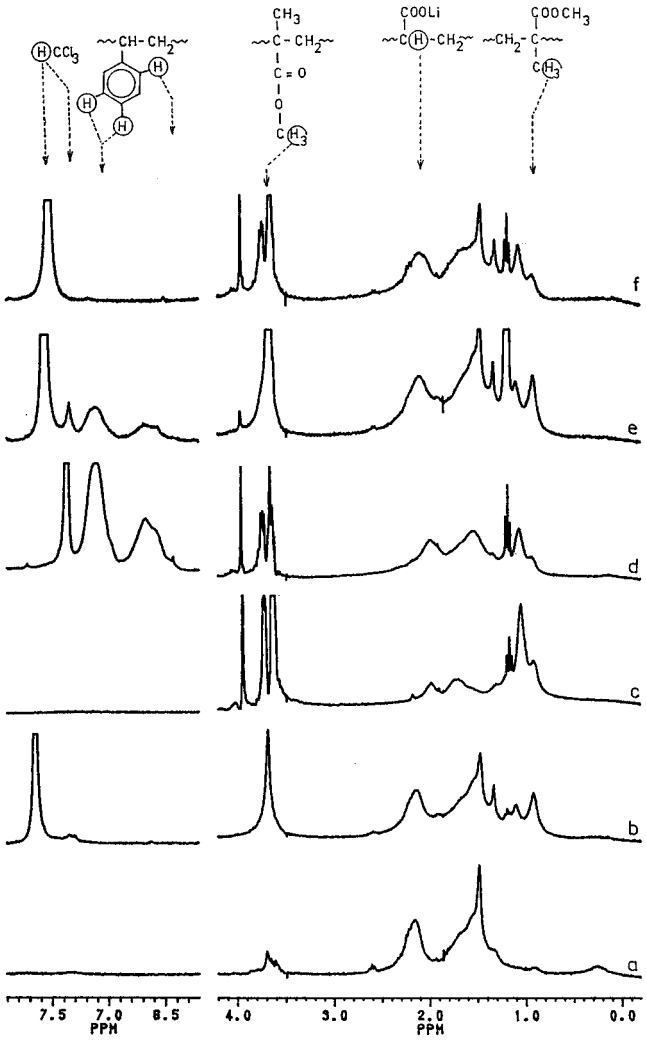



**Figure 9.** $^1H$ NMR spectra of (a) a 1.0% $D_2O$ solution of PMM−PAANa, (b) the same as (a) but after equilibrium solubilization with chloroform, (c) a 1.0% $D_2O$ solution of PS−PMANa, (d) the same as (c) but after equilibrium solution with chloroform, (e) solution (b) after mixing with 100% v/v excess of (c), (f) solution (d) after mixing with 100% v/v excess of (a).

micelles with PMMA cores. The exchange process is fast so that equilibrium was apparently reached in the first spectrum measured after mixing.

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