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Polymer Dynamics in an Interface-Confined Space: NMR Study of Poly(hexyl ethacrylate)-*block*-poly(acrylic acid) and Poly(dodecyl methacrylate)-*block*-poly(acrylic acid) Micelles in D_2O[†]

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ABSTRACT: The mobility of distant methyl side groups in poly(hexyl methacrylate)-*block*-poly(sodium acrylate) (PHMA−PAANa) and poly(dodecyl methacrylate))-*block*-poly(sodium acrylate) (PLMA−PAANa) micelles, dispersed in D_2O and characterized by SANS, was studied using ^1H single and double quantum high-resolution and MAS NMR. Transverse and rotating-frame relaxation was studied at temperatures 320−345 K in the original micellar solutions and in the systems with their viscosity gradually increased by additions of high-molecular-weight poly(ethylene oxide) and with the micellar cores gradually swollen by chlorobenzene. The relaxation data were quantitatively evaluated using a pragmatic model based on Cohen-Addad's theory. The results obtained strongly indicate that the side groups are relatively immobilized to an even higher degree than in poly(2-ethylhexyl acrylate)-*block*-poly(acrylic acid) micelles at the same conditions. The most immobilized groups are at or near the interface. Possible underlying effects, including penetration resistance of the surrounding water molecules, fixation of the polymer backbone at the interface, and motional correlation between the distant side group and the backbone are discussed.

Introduction

The problem of local and semilocal mobility of macromolecules in a restricted supramolecular space, in particular that confined by an hydrophobic/hydrophilic interface, is of an utmost importance for understanding the functional behavior of many molecular devices as well as natural organelles. This is given by the fact that such mobility not only affects the internal ordering of the given system but also influences its transport properties as well as its ability to react to changes in the external medium. Among the systems suitable for the study of such a problem, polymer micelles have a special appeal given by a relatively easy variation of their properties by purely synthetic means. This applies in particular to the micelles of amphiphilic block copolymers in water which have proven to be interesting objects of study[1−7] as examples of spontaneously self-assembled systems of macromolecules. In principle, a number of methods such as time-resolved fluorescence, dynamic light scattering, and NMR could be used for the study of molecular mobility in such systems. There are some obstacles to their use, however. Fluorescence spectroscopy needs the introduction of an bulky chromophore into a delicate molecular system. Dynamic light scattering is now able to use a deep analysis of the correlation times of different molecular motions. However, in the case of micelles, this applies to the micellar shell rather than to the core. NMR as a powerful probe into molecular dynamics also meets some stumbling blocks given by the motional restrictions of some interesting parts of the micelles. In recent years, some ways to augment the possibilities of NMR in this area have been found.[8−13] In addition to insight into the detailed structure of micelles, perhaps the most valuable information provided by NMR is that about the local and semilocal dynamics in an unperturbed micellar state.

In our recent study,[12] we have demonstrated a rather surprising effect of the core−shell interface on the segmental mobility in the core of poly(2-ethylhexyl acrylate)-*block*-poly(acrylic acid) micelles in D_2O. As we have shown, the degree of relative immobilization depends on the mean distance of the incident group from the interface and applies even to methyl groups at the ends of the flexible 2-ethylhexyl side groups. Such groups can be argued to be motionally almost independent of the main chain, at least in the relevant time-window of NMR relaxation. Therefore, the effect of their relative immobilization should be due to nonspecific confinement of the material in the restricted area of the core rather than to the correlation of motions near a fixed point as analyzed for branched and cross-linked polymers by Brereton[14,15] and in particular Cohen-Addad.[21,22] However, such explanation could be questioned on grounds of an insufficiently different flexibility of the poly(acrylate) chain and the side group in which, moreover, one of the methyl groups is only four bonds away from the main chain (counting the bonds with relatively low rotational barriers). In view of this possibility, we proceeded to a supplementary study of analogous micelles in which (i) the main poly(methacrylate) chain is substantially more rigid than the subchain of the side group, (ii) there is only one terminal methyl group in the side group, and (iii) the incident methyl

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group under scrutiny is separated from the main chain by six or even 12 flexible bonds. According to the usual view, these three features should suppress the direct correlation of motion between the end of the side group and the main chain as much as possible. The results obtained with such systems are presented here.

Experimental Section

Materials. Poly(hexyl methacrylate)-*block*-poly(*tert*-butyl acrylate) (PHMA−PtBA) was prepared by subsequent GTP of hexyl methacrylate and *tert*-butyl acrylate in THF at −60 °C using the method described earlier.[8] Poly(dodecyl methacrylate)-*block*-poly(*tert*-butyl acrylate) (PLMA−PtBA) was prepared by subsequent anionic polymerization of *tert*-butyl acrylate (tBuA) and dodecyl methacrylate (LMA) in THF.[13] First, tBuA was quantitatively polymerized at −78 °C using the 1,1-diphenyllithium−LiCl (1/10) initiating system. In the second step, LMA was added and the system was warmed to −23 °C. In each step of the synthesis, the polymers were examined by GPC to be sure of their narrow distribution of molecular weights. The block copolymers were purified by precipitation in methanol−water 3:1 (vol/vol) and after drying and analysis converted into the respective poly(hexyl methacrylate))-*block*-poly(acrylic acid) (PHMA−PAAc) and poly(lauryl methacrylate)-*block*-poly(acrylic acid) (PLMA−PAAc) polymers by a selective acidolysis[8] of their PtBA blocks.

The block copolymers PHMA−PAAc and PLMA−PAAc were converted into a micellar form by gradual dialysis of their THF solutions with water.[8] The obtained micellar solution in water was then freeze-dried at −20 °C, and the material obtained was dissolved, usually in a concentration of 5 g/L, in D_2O for NMR analysis. As both types of micelles exhibited a tendency to aggregation in the acid form of their shells, they were converted into a partially (60% for PHMA−PAAc) or fully (PLMA−PAAc) neutralized form by addition of a stoichiometric amount of NaOH. In the neutralized form, the micellar solutions of both PHMA−PAANa and PLMA−PAANa were sufficiently stable over a month.

NMR Measurements. The 300.13 MHz ^1H NMR spectra of mostly 0.5%w/w solutions of the block copolymers in D_2O (99.8% d) were measured with a Bruker Avance DPX 300 spectrometer using 0.01% by weight of sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) as external standard. Most of the methods of measurement and evaluation used were described in our previous paper.[12] In addition to them, T_2 measurements under gradual swelling of the core and selective $T_{1\rho}$ measurements were done using the following procedures: in the former case, the micellar solution in a NMR tube was overlayered with chlorobenzene and sealed. Standard T_2 measurements with 32 points using the CPMG sequence with the inter-pulse delay 1 ms were then done collecting 48 scans for each point; each measurement thus took 2 h and was followed by a 2 h delay. $T_{1\rho}$ measurements were done with the transmitter placed exactly on the resonance of the methyl signal. After the hard $\pi/2$ pulse (15.4 μs), the transmitter was switched to a lower power (equivalent to 1.0 to 2.5 kHz) and a $\pi/2$-shifted phase and a pulsed spin-lock sequence of the length needed followed. A total of 64 points a distance of 1 ms apart were measured, collecting, as a rule, 320 scans. Pseudo-solid echo and multiple pseudo-solid echo measurements were done using the sequences suggested by Cohen-Addad[21] with conditions analogous to T_2 measurements. ^1H NMR static, MAS and Hahn-echo MAS spectra were measured at 200 MHz with a Bruker Avance DSX 200 spectrometer at 298 and 333 K using spinning rates of 2, 4, 8, and 15 kHz. High-resolution ZrO_2 rotor with a HR spacer and KEL-F caps was used for MAS of liquid samples.

Small-Angle Neutron Scattering (SANS) Measurements. SANS measurements were performed using the time-of-flight small-angle neutron spectrometer YuMO at the IBR-2 pulse reactor in the Joint Institute for Nuclear Research, Dubna, Russia.[17] The solution was placed 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.[18] The methods of measurement and evaluation were fully described in our previous paper.[12] Number averages of all parameters obtained by SANS such as core radius, aggregation number, core volume and interface area per one chain are used throughout this paper.

Results and Discussion

General Characteristics of the Systems and Their NMR Behavior. Poly(hexyl methacrylate)-*block*-poly(acrylic acid) copolymer (PHMA−PAAc) used in this study had average polymerization degrees of the first (P_{n1}) and the second blocks (P_{n2}) at 182 and 1145, respectively, and the molecular weight polydispersity was $\eta = 1.21$. As its micelles in the acid form showed some tendency to self-aggregation, a form neutralized to 60% (referred to as PHMA−PAANa in this text) was used in most cases. In this form, the copolymer formed stable micelles of a fairly uniform size. The weight ratio of the hydrophilic and hydrophobic parts κ was 2.66, i.e., ideal for the given P_{n1}. In contrast to it, poly(lauryl methacrylate)-*block*-poly(acrylic acid) copolymer (PLMA−PAAAc) could be prepared, on grounds of reactivity, in a much shorter version only, $P_{n1} = 28$. In this case, κ was used in the value 2.05, i.e., $P_{n2} = 203$. The somewhat lower κ was chosen here to avoid the tightening effect of the hydrophilic shell on the core.[10] In this case, the polydispersity was excellent, $\eta = 1.12$. Despite the almost oligomeric nature of PLMA−PAAc, its micelles in the acid form were rather unstable and showed a strong tendency to self-aggregation. Therefore, a fully neutralized sodium form was used (referred to as PLMA−PAANa). In this mode, the micelles were stable and fairly uniform, but their core was considerably larger than most of chemically similar block copolymer micelles. As most of this study was devoted to PLMA−PAANa, these micelles were studied first by SANS. According to this method, the mean radius of the micellar core was $R_C = 8.9$ nm with polydispersity (or standard relative deviation of the core radius) lower than 20%. From this, it can be estimated that about 260 PLMA blocks formed one micellar core. If swollen by chlorobenzene, R_C increased to 10.5 nm at equilibrium; i.e., the volume increase of the core was 69%.

Because of the low concentration of the samples (0.5%) and signal broadening, only proton NMR spectra of sufficient quality can be obtained. Relevant parts of proton NMR spectra of both PHMA−PAANa and PLMA−PAANa at temperatures varied from 310 to 350 K are shown in Figure 1. The signals of α-CH and β-CH_2 of the PAANa blocks are designed as a and b, respectively. The aliphatic groups in the respective side groups are numbered starting with the O−CH_2, i.e., the terminal methyl groups in PHMA and PLMA have numbers 6 and 12, respectively. As seen, only signals of the shell (a and b) and of the groups distanced at least three methylenes and the carboxyl group away from the polymer skeleton in the core (i.e., 4−6 in PHMA and 4−12 in PLMA) are visible even at a elevated temperatures. All others are broadened beyond detection. Whereas the shapes of the signals of the micellar shell are affected by the neutralization degree[9] but very little by temperature, the signals of the terminal methyl and methylene groups in the side groups of the core blocks are progressively narrowed but also increased in absolute intensity. As we explained in our previous study,[12] this effect must be due to increased local, semilocal and also global mobility at higher temperature leading to a

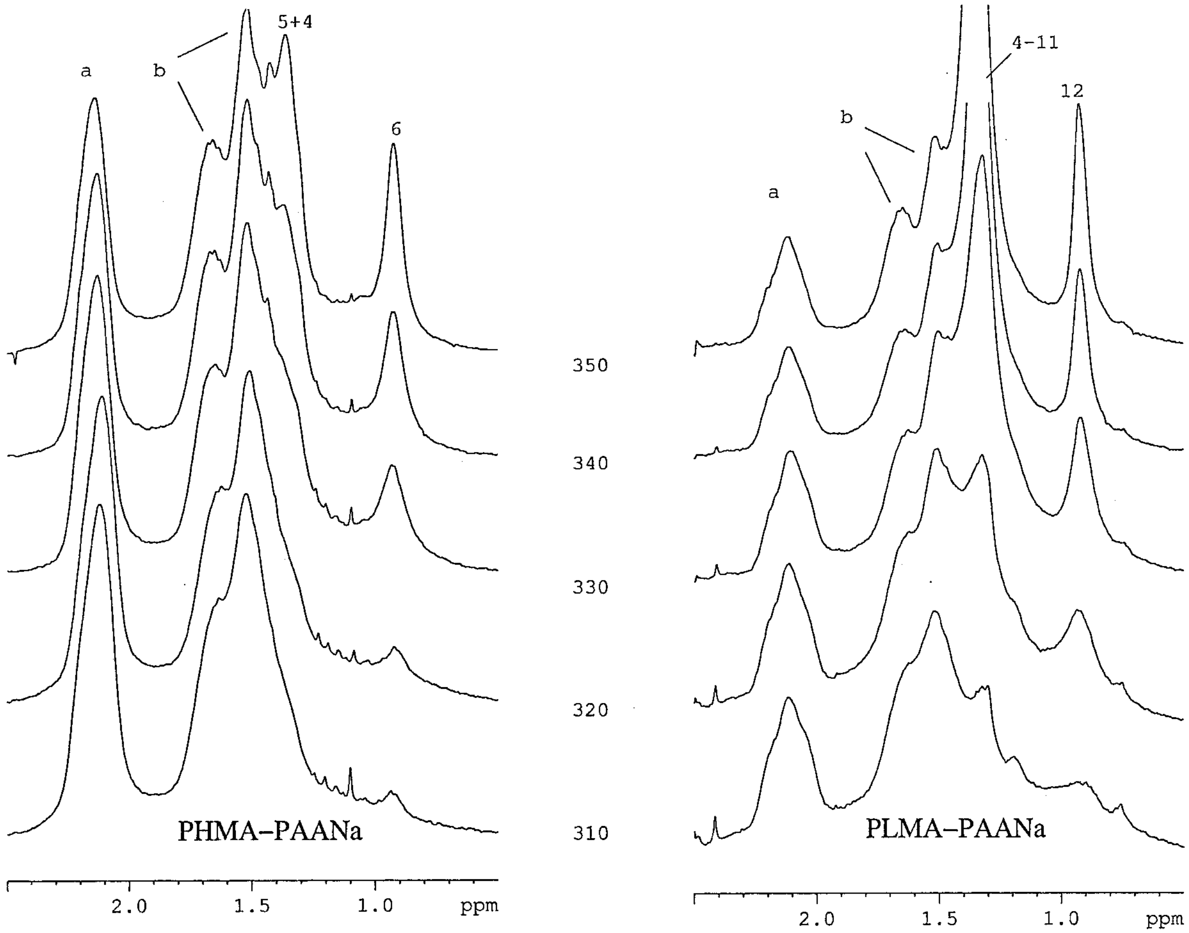

Figure 1. Relevant parts of 300.13 MHz ^{1}H NMR spectra of PHMA−PAANa and PLMA−PAANa (0.5% w/w in D$_2$O) at the indicated temperatures.

progressive canceling of residual static dipolar interactions.

The influence of the dipolar broadening on the shape and intensity of the signals is clearly illustrated in the MAS spectra measured with the solid-state NMR technique at 333 K. Because of a more effective excitation and recording of broad signals, a broad envelope of the signals appears in the spectra measured at low frequency magic angle spinning (MAS). This can be seen in Figure 2. At higher spinning rates, the broad components are gradually narrowed. Thus, MAS is as effective in removing static broadening as thermal motions are.

It has to be noted that the source of broadening are *not* the signals of the skeletal α-methyl and methylene protons which remain broadened beyond detection even under equilibrium swelling of the core with a good solvent. The methacrylate skeleton appears to be substantially rigid even in the case of the PLMA micellar core. The same applies for the parts of the side groups placed in the vicinity of the main chain.

The narrowing of the signals both by high-frequency MAS and by increased temperature indicate that at least a part of the signal broadening is caused[12] by residual static (mostly dipolar) interactions. In conformity with this, weak pseudo-solid spin echoes[21] were detected and slowing-down of transverse relaxation when measured using multiple pseudo-solid spin echo sequence[21] was observed. In addition, weak double and triple quantum filtered NMR signals of the methyl protons can be observed with both PHMA−PAANa and PLMA−PAANa. Because of the symmetry of the methyl group, multiple quantum coherence can develop only under perceptible motional anisotropy.[23−25] The corresponding residual static interactions can be progressively canceled by increased mobility due to thermal activation.

Discerning the Effects of Local, Semilocal, and Collective Motion on NMR Spectra. The effect of the frequency of micellar tumbling can be seen directly in Figure 3 where the spectra of 0.5% solution of PLMA−PAANa with various concentrations (0, 0.5, and 1.5%) of a high-molecular-weight poly(ethylene oxide) ($M_w = 6 \times 10^5$) are compared. PEO decreases the frequency of micellar tumbling by increasing the viscosity of the medium and probably by entangling with the micellar shell without interacting with the micellar core. As seen in Figure 3, decreasing frequency of micellar tumbling has a dramatic effect on the core signals. The broader components of the signals are progressively lost so that the integral intensity decreases and the remaining narrower components become apparent. At the highest viscosity, even the first signs of the triplet splitting of the remaining weak methyl signal can be observed (whereas most of this signal under normal conditions is not only broadened but also effectively decoupled by relaxation). The methyl signal obtained under normal conditions thus contains a variety of components with different line widths (and different relaxation rates), the narrower ones corresponding to sites with less hindered local motion and thus being also less sensitive to the overall micellar tumbling rate.

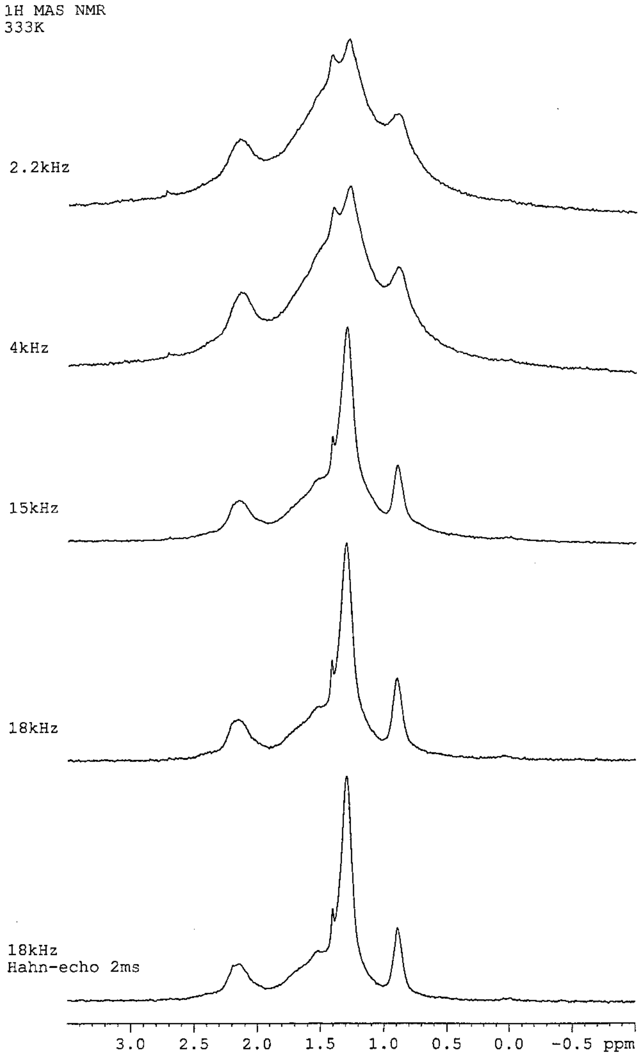

Figure 2. 200 MHz ^{1}H NMR MAS spectra of PLMA−PAANa (0.5% w/w in D_2O) at 333 K and indicated spinning frequencies.

The complementary experiment to that just described is swelling the core with a good solvent such as chlorobenzene. In this case, the micellar tumbling (which is mostly affected by the state of the micellar shell) remains virtually intact whereas the local and segmental mobilities in the core increase. As shown in Figure 4, core swelling has the same effect as a temperature increase.

Thus, substantial barriers of isotropic motion even of the parts of the side groups distant from the main chain must exist in both types of micelles, in sharp contrast to the corresponding PHMA and PLMA homopolymers (which are both viscous liquids and have well-resolved spectra in bulk at 330 K). These barriers are different (in height or population) for different positions of the groups in the core leading thus to different relaxation behavior documented by progressive signal narrowing in a T_2-filtering experiment[12] and polyexponentiality of the corresponding transverse relaxation curves.

Transverse Relaxation in the Intact State. The distribution curves of the different $T_{2\mathrm{i}}$ components constructed under the assumption

$$M(t) = M(0)\exp(-t\sum_i w_i T_{2i}^{\ -1}) \tag{1}$$

and in an analogous way to that in our previous paper[12] for the methyl signal of PHMA−PAANa and PLMA−PAANa at 330 K are given in Figure 5. The curves obtained by a two-dimensional Fourier transform are qualitatively analogous. Closely similar to them are also distribution curves (with T_{2i} substituted by $T_{1\rho i}$) obtained from $T_{1\rho}$ experiments using lower intensities of the spin-lock field. Their gross features can be considered credible and reflecting a striking analogy in relaxation behavior of PEHA−PAANa reported recently[12] and both types studied here. Although the curve of PLMA−PAANa is somewhat shifted to longer relaxation times (higher mobilities), it also contains a considerable population of components with very short relaxation times.

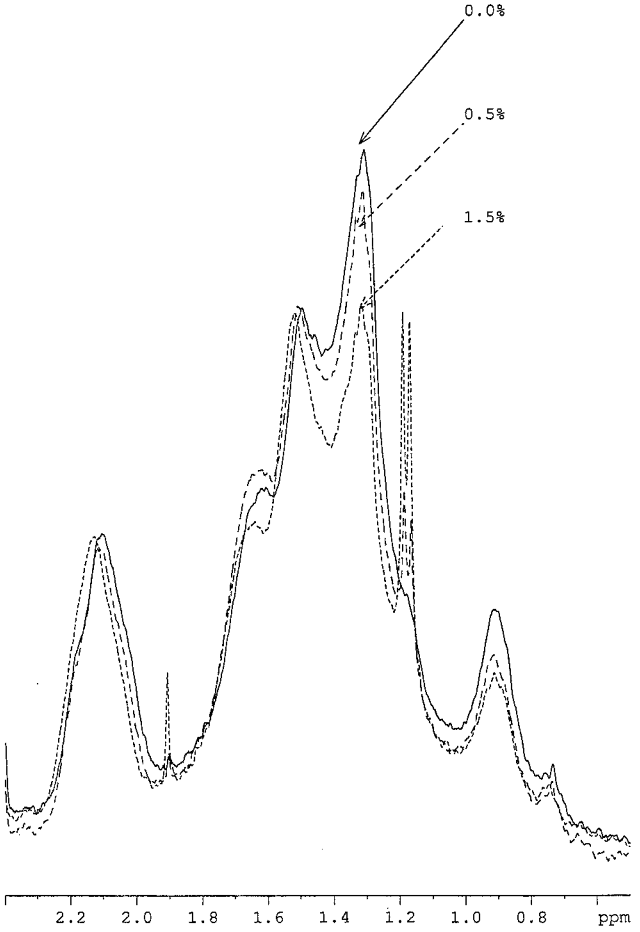

Figure 3. Relevant parts of 300.13 MHz ^{1}H NMR spectra of PLMA−PAANa (0.5% w/w in D_2O) in the presence of indicated concentrations of poly(ethylene oxide) ($M_w = 6 \times 10^5$) at 330 K.

The total lack of motional correlation of the distant parts of the PLMA side groups on the rest of the chain is clearly refuted by Figure 6 where the spectra of PHMA−PAANa and PLMA−PAANa are compared to that of PHMA−PAANa swollen with an approximately equimolar amount of hexane. Thanks to their slightly different chemical shift, the signals of hexane can be seen to be incomparably narrower, i.e., the mobility of the corresponding groups higher than in PLMA−PAANa. The analogous signals of PHMA−PAANa are relatively narrowed and gain intensity, compared to PLMA−PAANa. Hence, the presence of the low-molecular-weight hexane increases the mobility of the corresponding groups much more than that of a bound hexyl group.

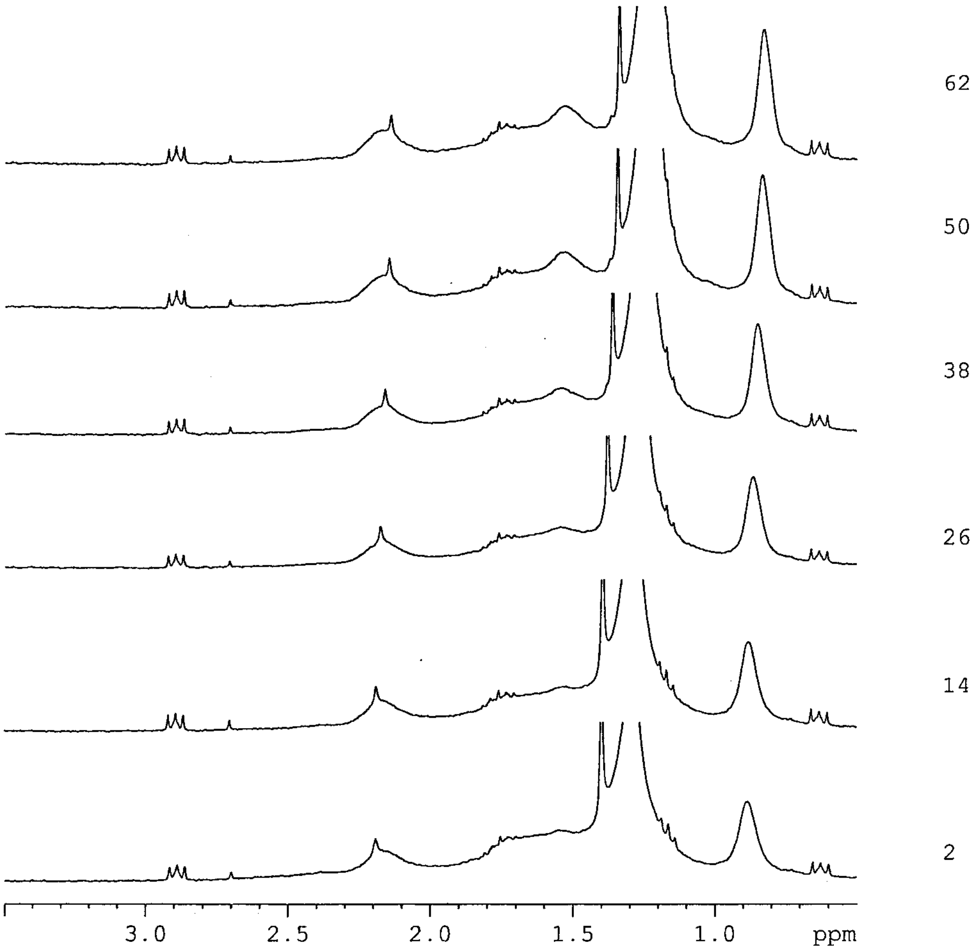

Figure 4. Relevant parts of 300.13 MHz ^{1}H NMR spectra of PLMA−PAANa (0.5% w/w in D_2O) progressively swollen by diffusing chlorobenzene (time in hours indicated).

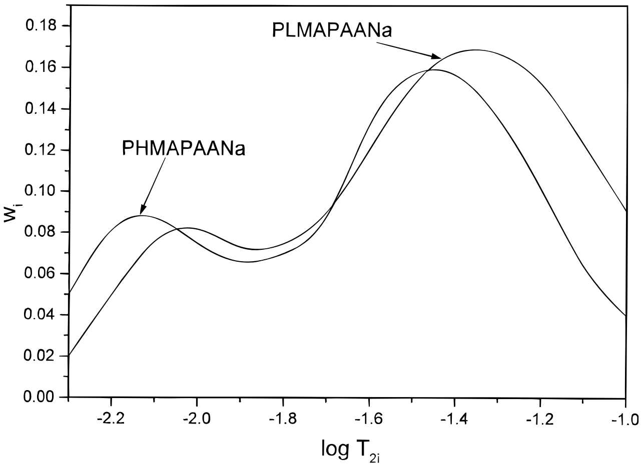

Figure 5. Reconstructed normalized distributions of transverse relaxation times of the terminal methyl signal in the side group of PHMA−PAANa and PLMA−PAANa at 330 K.

Radial Dependence of Mobility in a Gradually Swollen Core. On the basis of this behavior, the most correlated and effectively immobilized side groups should be expected near to the core−shell interface[12] where the polymer backbone has a fixed position. As the interface area corresponding to one inter-block link is about 420 Å^2, there must be numerous contacts of the side groups with the interface leading to additional motional restrictions due to the osmotic pressure of water molecules. To explore this, we have studied the evolution of transverse relaxation rate of the methyl signal of PHMA−PAANa and PLMA−PAANa under gradual swelling of the core by chlorobenzene which is known to form a relatively narrow diffusion front.[10] To avoid ambiguities of polyexponential fit we fitted a biexponential function

$$M_x(t) = M_x(0)[w_1 \exp(-t/T_{21}) + (1 - w_1) \exp(-t/T_{22})] \tag{2}$$

to the transverse magnetization decay. The results obtained at 330 K for PHMA−PAANa are given in Figure 7 and those for PLMA−PAANa in Figure 8. As seen in both cases, the relative population of the fast relaxing component and the corresponding relaxation rate decreases mostly in the early stages of the swelling whereas the relaxation of the other component slows down more apparently in its later stages. A plausible explanation of this behavior is a radial dependence of relaxation rates, i.e., relative immobilization of the side groups placed nearer to the interface.

A notable byproduct of this investigation is the relaxation polyexponentiality even in the equilibrium-swollen state indicating that some correlation and/or restriction of motion remains at the interface and near to it.

Transverse Relaxation at Different Temperatures: Semiquantitative Evaluation. Finally, to explore the motional hindrances in the core, we investigated the relaxation behavior of the methyl signal in

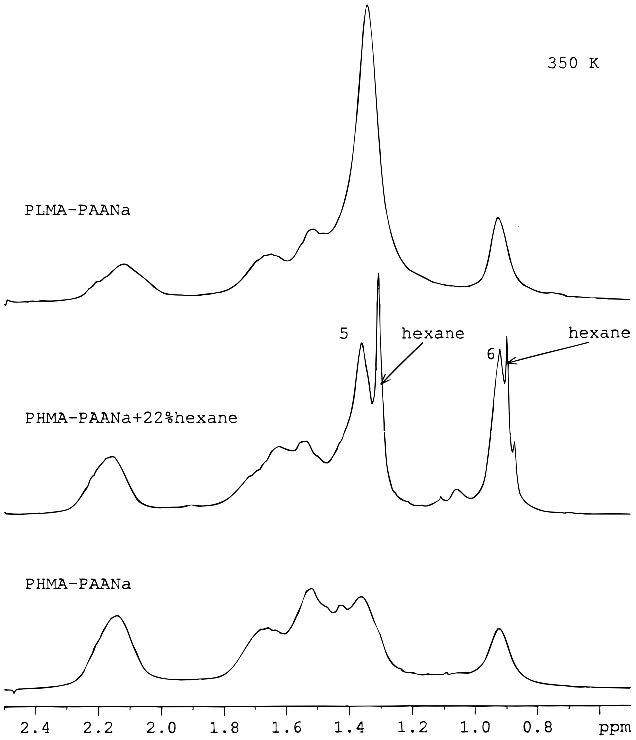

Figure 6. Comparison of 300.13 MHz ^{1}H NMR spectra of PHMA−PAANa and PLMA−PAANa with that of PHMA−PAANa with its core swollen by hexane (total 22% w/w of the whole micelle).

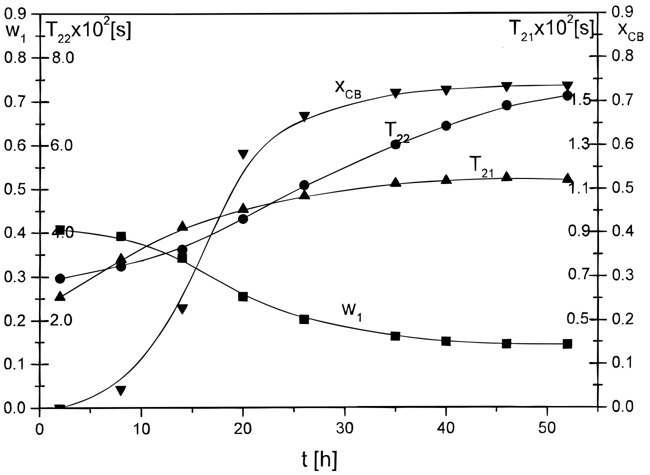

Figure 7. Evolution of transverse relaxation time components T_{21} (normalized weight w_1) and T_{22} (weight $1 - w_1$) at the indicated weight fraction of chlorobenzene swollen into the micellar core of PHMA−PAANa (330 K).

PLMA−PAANa at various temperatures. The decay curves of absolute intensities, normalized to the starting intensity at 320 K, are given in Figure 9. We interpret the shown complex behavior using an approximate model based on the Cohen-Addad's treatment[22] of the Rouse model and described in Appendix A. Central to this model is the relation

$$M_x(t) = M_x(0)\sum_i w_i \exp\left\{-\frac{\omega_D{}^2\tau_{ci}{}^2}{1 + (\omega_D\tau_{ci}\tau_R)^{-2}}[t/\tau_{ci} + \exp(-t/\tau_{ci}) - 1]\right\} \quad (3)$$

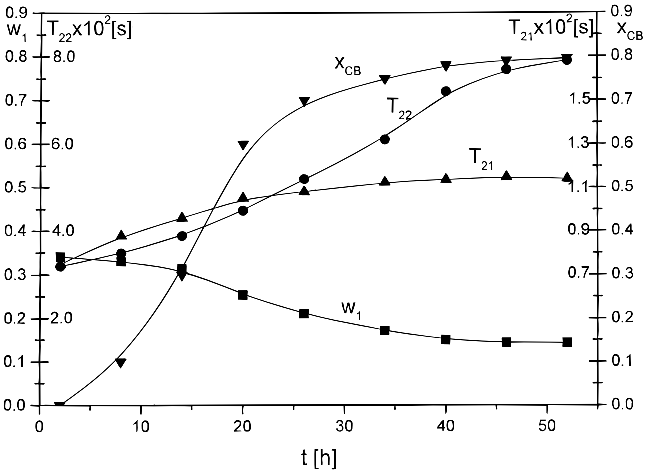

Figure 8. The same plot as in Figure 7 but for PLMA−PAANa.

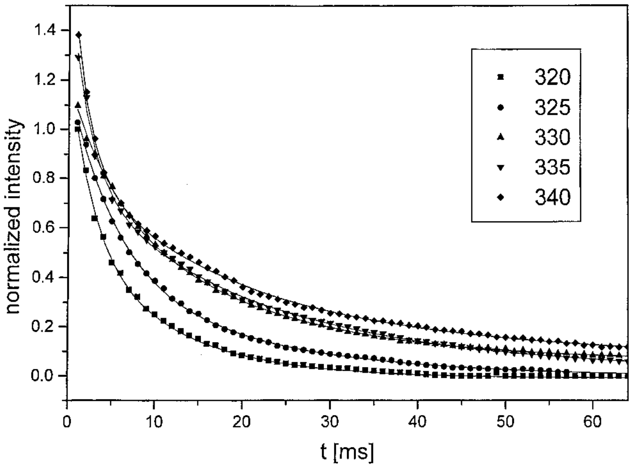

Figure 9. Full transverse relaxation curves of the methyl signal of PLMA−PAANa at the indicated temperatures.

Table 1. Best Fit[a] of Dynamic Parameters for PLMA−PAANa

					τ_i, s × 10^{-7}		T_{2i}*, s × 10^{-3}	
layer	w_i	R_{ci}/R_c	τ_0, s	ϵ_i/k, K × 10^3	330 K	345 K	330 K	345 K
a[b]	0.045	0.98	1.28 × 10^{-20}	11.85	508	106	0.2	2.3
b[b]	0.122	0.94	2.56 × 10^{-19}	10.73	339	82	0.3	3.0
c[b]	0.119	0.89	6.89 × 10^{-17}	8.56	127	41	0.6	6.1
d	0.348	0.72	2.11 × 10^{-14}	5.83	9.9	5	31.2	52.8
e	0.366	0	4.74 × 10^{-11}	3.72	3.7	2	57.2	105.5

[a] The values used: 2.25 × 10^4, $\tau_R(330) = 1.99 \times 10^{-5}$ s, and $\tau_R(345) = 1.32 \times 10^{-5}$ s. [b] Below 335 K, the corresponding signal components were assumed to be unobservable due to residual static broadening.

with the normalized statistical weight w_i and effective correlation time τ_{ci} (correlated with the local and semilocal motion) of the ith group, respectively, and the correlation time τ_R of isotropic tumbling of the micelle. Both τ_{ci} and τ_R are supposed to be exponentially dependent on temperature. A heuristic approach to the fitting, described in Appendix B, was used. The results are given in Table 1. The signal shapes simulated using the model with the fitted values of w_i and τ_{ci} and assuming Lorentzian shapes (the Gaussian components decay much faster and make only a small contribution to the signal) agree well with those of the deconvoluted experimental signal 12 at different temperatures.

The values of ϵ_i, interpreted as the mean effective barriers of motion and expressed in molar dimension, range from 30.3 to 96.5 kJ/mol. They are rather high compared with the usual barriers of single rotations in vacuo or low-viscous media, which usually do not exceed 20 kJ/mol. As indicated by our previous results[12] and the present swelling experiments, the groups with lowest mobility (or highest ϵ_i/k) are those nearest to the interface. Table 1 shows that the groups **a** having highest effective barrier of free motion are indeed placed in a very thin layer. Calculated from the respective value of w_i, $R_{ci}/R_c = 0.98$ (R_c and R_{ci} being the core radius and the inner radius of the given layer), i.e., the layer is 1.78 Å thick. Considering the interface area corresponding to one inter-block link of about 420 Å^2, it is reasonable to conclude that this layer must be formed by the first side groups of the hydrophobic block spread over the interface and consequently most affected by it. The calculated thickness of the next layer ($R_{ci}/R_c = 0.94$) is about 4 Å, with the average area in the middle of the layer 353 Å^2/chain, i.e., 2−3 monomer units next nearest to the interface can be placed here. On the other hand, groups **d** and **e** are at least 9.5 Å distanced from the interface and thus influenced by it only indirectly. Accordingly, they exhibit distinctly higher mobility. Even their relaxation rate is distinctly higher than that of the analogous groups in the bulk polymer ($T_2 = 0.26$ s at 330 K), however. It has to be admitted that the distinction between layers, in particular those in the group **c**−**e**, is related to the method of analysis and serves mostly illustrative purposes.

Conclusions. We have shown that the relative side group immobilization observed earlier in the cores of polyacrylate-*block*-poly(acrylic acid) micelles[12] is even more pronounced in the cores of polymethacrylate-*block*-poly(acrylic acid) such as PHMA−PAANa and PLMA−PAANa where the motional correlation between the polymer backbone and a distant side group was expected to be less pronounced. Three distinct, if related, phenomena can be discerned in this connection: (i) the relative immobilization of the side groups at or near the interface; (ii) the even more pronounced immobilization of the polymer backbone in the micellar core; and (iii) the apparent partial correlation of the mobility of a distant side group with that of the polymer backbone. As we have pointed out in our previous study,[12] point i (and partly points ii and iii) can be explained by the cohesive resistance of the surrounding water molecules to the penetration of a hydrophobic group, which is needed for its isotropic motion. The effect is subtle but substantial as seen from the comparison of $\epsilon_{\mathbf{a}} - \epsilon_{\mathbf{e}}$ (66.2 kJ/mol) with the activation energy of viscosity of water (21.8 kJ/mol). Phenomenon ii should be partly due to the same origin. However, an additional and perhaps more important factor can be the fixation of the backbone at the point of its link with the hydrophilic block and maybe even at the center of the core. An interesting and from the point of view of general physical chemistry maybe most important phenomenon is point iii. As shown above (cf. Figure 6), the dynamic behavior of the inner-core side groups cannot be explained simply in terms of viscosity of a medium increased by its fortification with relatively stiff polymer backbones. Even a methyl group distanced by 12 flexible groups from the backbone behaves in an utterly different way than an analogous group in a low-molecular-weight compound does. We thus have to admit a necessary, if subtle, correlation of motion of even a distant but bound group with that of the polymer backbone. In a system with an interface-restricted space, this effect is amplified by the need of the side groups to correlate their motions mutually (at least to some degree) and thus to mediate the correlation even with the backbones to which they are not directly bound. Hence the space restriction reveals subtle motional correlation even in apparently disordered systems.

Appendix A: Model of Transverse Relaxation in the Micellar Core

Let $M_{xi}(t)$ be the transverse magnetization of the nucleus in the end group of the ith side group of the hydrophobic block in the core. Even under assumption of mutual statistical independence of the local motion, skeletal motion and micellar tumbling, the time dependence of $M_{xi}(t)$ must be complex.[12,16−23] Any model simple enough to be of use in analyzing the experimental data must be rather pragmatic. In some contrast to our previous attempt[12] to adopt the Lipari−Szabo approach,[16,19,20] we base our present model on the most comprehensive treatment of the relaxation in polymers given by Cohen-Addad.[22] Starting from the Rouse model of the motion of the given side group and using the notation ${\tau_{pq}}^{-1} = {\tau_p}^{-1} + {\tau_q}^{-1}$ where τ_p is the correlation time of the pth motional mode, $M_{xi}(t)$ can be approximated[22] by

$$M_{xi}(t) = M_{xi}(0)[\sum_{pq} \exp\{-{\omega_{\mathrm{D}}}^2{\tau_{pq}}^2[t/\tau_{pq} + \exp(-t/\tau_{pq}) - 1]\}]_i \quad \text{(A1)}$$

where $\omega_{\mathrm{D}}2$ is the second moment given by the actual mean static dipolar interactions. We introduce an *effective* correlation time of the ith group τ_{ci} such that the sum in eq A1 can be expressed by one exponential. Further, we assume (in accord with experimental data[22]) that the static dipolar interactions are reduced by a factor $1/(1 + {\kappa_i}^2{\omega_{\mathrm{D}}}^{-2}{\tau_{\mathrm{R}}}^{-2})$, τ_{R} being the correlation time of the isotropic micellar tumbling. Assuming that the transverse magnetization decays as a weighted sum of the decays of individual groups, we obtain the expression

$$M_{\mathrm{x}}(t) = M_{\mathrm{x}}(0)\sum_i w_i \exp\left\{-\frac{{\omega_{\mathrm{D}i}}^2{\tau_{\mathrm{c}i}}^2}{1 + {\kappa_i}^2{\omega_{\mathrm{D}i}}^{-2}{\tau_{\mathrm{R}}}^{-2}}[t/\tau_{\mathrm{c}i} + \exp(-t/\tau_{\mathrm{c}i}) - 1]\right\} \quad \text{(A2)}$$

where w_i is the statistical weight of groups with the same decay rate. The temperature dependence of $\tau_{\mathrm{c}i}$ is assumed to be exponential

$$\tau_{ci} = \tau_{\mathrm{c}i0} \exp(\epsilon_i/kT) \quad \text{(A3)}$$

ϵ_i being the corresponding activation energy of the motion. That of τ_{R} is given by the expression

$$\tau_{\mathrm{R}} = \frac{4\pi R^3\eta_0 \exp(\epsilon_{\mathrm{v}}/kT)}{3kT} \quad \text{(A4)}$$

where R is the effective radius of the spherical micelle, η_0 and ϵ_{v} are the preexponential factor and activation energy of the medium's viscosity, and k and T are the

Boltzmann constant and temperature, respectively. In eq A2, $(\omega_{\mathrm{D}i}/\kappa)^2$ is the measure of the residual static dipolar interactions; we use $\kappa = 1.0$.

Equations A2, A3, and A4 form our model fitted to the experimental curves. Because of the level of approximation, the values of $\tau_{\mathrm{c}i}$ and ϵ_i are rather phenomenological factors describing the local and semilocal dynamics.

Appendix B: Heuristic Simulation and Fitting

The procedure was as follows: (i) as the simplest possible set able to describe the observed decay curves, five signal components with gradually increasing ϵ_i (or $\tau_{\mathrm{c}i}$) were assumed; (ii) trial values of $\tau_{\mathrm{c}i}$ were chosen, pseudo-T_{2i} values expressed as

$$T_{2i}{*} = [1 + (\omega_{\mathrm{D}i}\tau_R)^{-2}]/\omega_{\mathrm{D}i}{}^2\tau_{\mathrm{c}i} \qquad \text{(B1)}$$

calculated, and components with $T_{2i}{*} < 5 \times 10^{-4}$ s assumed to have a vanishing contribution to M_x even at $t = 0$; (iii) trial values of w_i were chosen, renormalized according to (ii), transverse decay simulated, and if near to the actual decay, the values of $\tau_{\mathrm{c}i}$ were fitted using eq 3; (iv) from the logarithmic dependence of $\tau_{\mathrm{c}i}$ on T, $\tau_{\mathrm{c}i0}$ and ϵ_i values were derived and these re-fitted to the whole collection of decay curves.

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