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13. ABSTRACT (*Maximum 200 words*)

Deuterium NMR relaxation measurements have been used to probe the dynamics of specifically labelled poly(styrene-co-vinyl pyridine) in solution and on silica. Of particular interest in this study was the comparison of the dynamics of the adsorbed polymers on silica with those of the block copolymer and homopolymer in solution. We found that in toluene, the styrene segments on the surface-bound polymer had *enhanced* mobility over that in toluene solution. This enhanced mobility does not extend to the other solvent systems tested (CCl_4 and CCl_4/CH_3OH). For the latter systems, the styrene mobility on the surface bound-polymer was lower than those of the corresponding solutions, as expected. Thus we conclude that this enhanced mobility probably occurs only in the presence of thermodynamically good solvents for styrene. A comparison of lower molecular weight (10 kg/mol) block copolymer and styrene homopolymer were also made in toluene. These results were interpreted through the use of the Hall-Helfand model for chain dynamics as indicating limited aggregation of the block copolymer in solution.

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Dynamics of Block Poly(styrene-co-vinyl pyridine) (SVP) in Solution and on Silica

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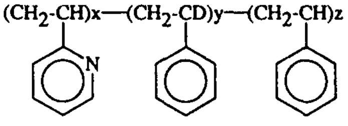
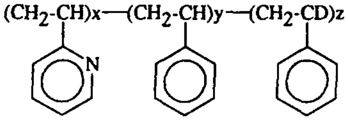
Introduction

We are continuing our studies of the dynamics of block copolymers on surfaces and in solution using NMR spectroscopy. Of special interest to us has been the behavior of copolymers (or terpolymers) made from styrene and vinyl pyridine. We have previously shown that in toluene, poly-(styrene-co-vinyl pyridine) adsorbs to silica via the vinyl pyridine groups.[1] Furthermore, in toluene, the styrene segments are extended into the solution at about 4x their normal radius of gyration in agreement with previous surface forces measurements.[2] The density profile was also in agreement with the parabolic one presented by Milner, et al. [3] This work was based on the use of deuterium NMR on the VPDSS and VPSDS block (ter)polymers shown below. These polymers have deuterium labels on the backbone of the styrene segments.



VPDSS



VPSDS

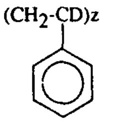
More recently we have extended these studies to different solvent systems where the thermodynamic quality of the solvent is poorer for styrene. Specifically, we have probed the NMR behavior in carbontetrachloride and carbontetrachloride/methanol mixture.[4] While the presence of methanol gives additional motional freedom to the bound - VP segments, both solvent systems were found to significantly limit the motional freedom of the styrene segments, as compared to their behavior in toluene.

In the present paper, we focus on the motional *dynamics* of the polymers as measured through deuterium NMR spectroscopy. Specifically, we compare the dynamics of the adsorbed polymers on silica with the behavior of block copolymers and homopolymers in solution. Both higher and lower molecular weight homopolymers have been probed.

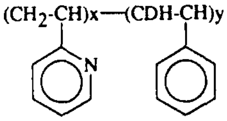
Experimental

The synthesis of the VPSDS and VPDSS terpolymers have already been described.[1] The monomers, α-deuteriostyrene and β-deuteriostyrene were prepared from α- bromostyrene or β-bromostyrene by adding D_2O to a Grignard product with Mg metal. The yields of the products were 70-80%. The level of deuteration was typically 80-90% as determined by deuterium and proton NMR.

Both α-deuteriopolystyrene(α-DS) and β-deuteriopoly-(styrene-co-2-vinylpyridine) (β-DSVP) were prepared by anionic polymerization. Synthesis of α-deuteriopolystyrene was conducted in a solution of cyclohexane using sec-butyllithium as initiator with 30 wt% monomers at 0 °C for 1hr. β-deuteriopoly(styrene-co-2-vinylpyridine) was made in THF instead of cyclohexane because of the insolubility of 2-vinylpyridine in cyclohexane. The reaction was initiated at room temperature then cooled down to -78 °C, β-deuteriostyrene was added first followed by 2-vinylpyridine. The resulting polymers are shown along with their designation. We note that the VPDS is labelled in the methylene position.



DS-4



VPDS-B

The molecular weights of polymers as determined by GPC are given in Table I and are based on polystyrene standards.

Table I. Molecular Weights of Polymers

Polym.*	M_w (kg/mol)	PD	wt. %S
DS	265.5	2.5	100
DS-4	10.0	1.15	100
VPDSS	19.2	1.5	37.5D/37.5H
VPSDS	21.3	1.4	37.5D/37.5H
VPDS-B1	9.8	1.76	77

*where the B designation denotes that the deuteron is in the β-position (the others are all α).

Solutions for NMR studies were prepared using distilled solvents. Degassing was not necessary because of the shortness of the relaxation times. Deuterium NMR T_1, T_2 measurements were performed on a Varian VXR-200 spectrometer at 30.7 MHz for deuterons. In all cases, the decay curves could be characterized by a single-exponential relaxation time. The relaxation times were calculated from signal heights using a log linear least-squares fit, the experimental errors in the relaxation time measurements were estimated to be less than 5%.

NMR Relaxation

Before discussing the NMR data, it is appropriate to note that the deuteron relaxation rates are due to the reorientation of the deuterium nucleus relative to its principal electric field gradient axis. Fortunately, this is along the C-D bond axis so that the relaxation rates give information directly on the C-D reorientation. The general expression for the deuterium quadrupolar relaxation in liquids is well-known [5] and given by:

$$1/T_1 = (3\pi^2/20)(e^2qQ/h)^2\,[J_1(\omega_0) + 4J_2(2\omega_0)] \tag{1}$$

and

$$1/T_2 = (3\pi^2/40)(e^2qQ/h)^2\,[3J_0(0) + 5J_1(\omega_0) + 2J_2(2\omega_0)] \tag{2}$$

where e^2qQ/h is the quadrupole coupling constant, 165KHz based on the solid-state deuterium spectrum of bulk polystyrene-d.

In order to interpret the relaxation times in terms of a motional mechanism, the Hall-Helfand (HH) [6] model has been used with some success and the spectral density given by [7]:

$$J(\omega) = 2A(\omega)\,\{[\lambda_0(\lambda_0 + 2\lambda_1)-\omega^2]^2 + [2(\lambda_0 + \lambda_1)\omega]^2\}^{-0.25} \tag{3}$$

where

$$A(\omega) = \cos\{0.5\tan^{-1}[(2(\lambda_0+\lambda_1)\omega)/(\lambda_0(\lambda_0+2\lambda_1)-\omega^2)]\}. \tag{4}$$

where λ_0 is the single-bond conformational transition rate, λ_1 is the cooperative conformational transition rate which involves several bonds.

Results and Discussion

Surface and Solution States

Carbon-13 NMR spectra of the VPDSS and VPSDS polymers on silica show narrow resonances for styrene and broader resonances for the vinyl pyridine groups for the surface-bound material when swollen with toluene. This is indicative of the mobilities in the two different groups in the polymer. Deuterium NMR relaxation times on the surface bound systems provide a way to quantify this phenomena in terms of rates for segmental reorientation through the HH model. However, there is a simpler way to compare the behavior of these polymers. Namely, by taking the ratio of the relaxation times T_1 and T_2. For small molecules which move isotropically, the T_1/T_2 ratio is typically 1. For high molecular weight polymers dominated by local segmental motions, the ratio can be much greater than one.[7] Listed in Table II are these values for the VPSDS and VPDSS polymers on the surface and in solution at 18°C.

Table II. Relaxation Time Values for VPDSS and VPSDS Polymers at 18 °C

Polym.	Solv.	T_1(ms)	T_2(ms)	T_1/T_2	State
VPDSS					
	toluene	3.63	3.38	1.07	surface[a]
	toluene	3.63	2.75	1.32	solution[a]
	CCl_4/CD_3OD	2.66	1.83	1.45	surface[b]
	CCl_4	3.05	1.78	1.71	surface[b]
VPSDS					
	toluene	3.94	3.60	1.09	surface[a]
	toluene	3.94	3.25	1.21	solution[a]
	CCl_4/CD_3OD	3.44	2.89	1.19	surface[b]
	CCl_4	3.30	2.02	1.63	surface[b]

[a] From reference 1.
[b] Interpolated to 18 °C from temperature-dependent data.

As is evident from Table II, the lowest ratio is for the surface systems swollen with toluene. In fact the ratio for this system is even higher than in solution. This means that compared to solution, the mobility of the surface-bound styrene segments is greater in toluene. The enhanced mobility on the surface does not extend to the other solvent systems as their ratios on the surface are greater than those in solution.[4]

Homopolymer and Block Copolymer in Solution

The results of deuterium NMR relaxation studies on the DS-4 and VPDS-B1 at 25 °C are reported in Table III. To date, only a limited concentration range has been studied. We note that these are low molecular weight species (ca. 10 kg/mol) and that the relaxation time ratios are closer to 1 than for the higher molecular weight polymers previously studied.

Table III. Solution Relaxation Data for Deuterated Copolymers in Toluene.

Polym.	Conc.(wt%)	T_1(ms)	T_2(ms)	T_1/T_2
DS-4	6.59	5.10	4.77	1.07
	14.18	4.63	4.27	1.08
	20.35	4.29	3.90	1.10
	26.07	4.01	3.61	1.11
	34.16	3.57	3.11	1.15
VPDS-B1	7.74	4.56	4.13	1.10
	14.91	4.21	3.72	1.13

The relaxation data for both homopolymer and block copolymer decrease with increases in concentration. The concentration dependence for T_2 is greater than that for T_1. It is interesting to note that the two kinds of polymers have small, but measurable differences with the block copolymer of similar molecular weight and concentration having the shorter relaxation times. In this regime, a shorter relaxation time is indicative of more restricted motion. We believe that this is due to the tendency of the block copolymer to associate, possibly even in micelles. However, for these molecular weights, the effect is small. Aggregation of the VP groups would be consistent with their thermodynamically poorer interaction with toluene.

Table IV. Hall-Helfand Parameters for the Low Molecular Weight Polymers in Toluene.

Conc.(wt%)	$J_0(\omega)$[a]	$J_1(\omega)$[a]	$J_2(2\omega)$[a]	λ_0[b]	λ_1[b]	λ_1/λ_0
DS-4						
6.59	10.9	10.5	9.5	6.30	23.8	3.8
14.18	12.2	11.7	10.5	5.62	20.9	3.7
20.35	13.5	12.8	11.2	5.07	18.9	3.7
26.07	14.7	13.8	12.0	4.78	16.9	3.5
34.16	17.5	16.1	13.4	3.97	14.5	3.6
VPDS-B1						
7.74	12.8	12.1	10.6	4.89	22.4	4.6
14.91	14.5	13.4	11.4	4.19	20.6	4.9

[a] in units of 10^{-10}s.
[b] in units of 10^{+8} s^{-1}.

In order to quantify the dynamics of these species, we have fit the relaxation data to the HH model to describe the motions of the polymers and the results are shown in Table IV. Space does not permit the detailed description of the spectral density results. Instead, we focus on the transitional probabilities given by λ_0 (single-bond conformational transition rate) and λ_1 (cooperative conformational transition rate involving several bonds). The ratio λ_1/λ_0 for the block copolymer samples are greater than that for homopolymer samples. We believe that this is indicative of slower long range motions in the block copolymer consistent with the notion that these polymers aggregate. Further studies need to be performed to determine the extent of this aggregation and its dependencies on system variables.

Conclusions

The styrene segments on the block copolymer bound to silica, swollen with toluene, exhibit enhanced mobility over the same material in solution. This unexpected behavior appears to be limited to the thermodynamically good solvent and does not occur in the other solvent system studied. In solution, the NMR relaxation time measurements are consistent with aggregation of the copolymers even at these relatively low molecular weights.

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