i 20 - 20 - 20 - 20 - 20 - 20 - 20 - 20 -				1	OM8 NO. 0704-0188
		average 1 hour per r ng the collection of in to Washington Heat of Management and B	esponse, including the tir iformation. Send comme squarters Services, Directi ludget, Paperwork Reduc	ne for reviewing ins nts regarding this bi prate for informatio lion Project (0704-01	tructions, searching existing data sour urden estimate or any other aspect of in Operations and Reports, 1215 jeffer 88), Washington, DC 20503
	7/8/94	ATE	3. REPORT TYP 1/1/93 -	e and dates 7/8/94	COVERED
TITLE AND SUBTITLE				5. FUN	DING NUMBERS
NMR Studies of Pol	lymers at Inte	rfaces		PE-	N0014-91
AUTHOR(S)				PR-	1274
Frank D. Blum		C ELE	5,199 4	Ň	
PERFORMING ORGANIZATIO	N NAME(S) AND ADD	R		8. PERF	ORMING ORGANIZATION
University of Miss	ouri-Rolla			REPC	JKI NUMBEK
Department of Chem Rolla, MO 65401	istry		an a	J UMR	R-FDB- 41
ATTN: Frank D. Blu	m				
SPONSORING / MONITORING	AGENCY NAME(S) A	ND ADDRESS(ES)		10. SPO AGE	NSORING/MONITORING NCY REPORT NUMBER
Office of Naval Re Chemistry Division	search - Code	5000			
800 Quincy Street					
Arlington, VA 222	17				
ATTN: Kenneth J. W SUPPLEMENTARY NOTES	vnne				
				_	
For publication in	Polymeric Ma	terials Sci	lence and Eng	gineering	
a. DISTRIBUTION / AVAILABIL	ITY STATEMENT			12b. DI	STRIBUTION CODE
a. DISTRIBUTION / AVAILABIL	ITY STATEMENT		<u> </u>	12b. DI	STRIBUTION CODE
a. DISTRIBUTION / AVAILABIL	ity STATEMENT	ted public	release o	12b. DI	STRIBUTION CODE
a DISTRIBUTION/AVAILABIL Unlimited - Approv	red for unlimit	ted public	release 86	126. DIS	
a. DISTRIBUTION / AVAILABIL Unlimited - Approv	red for unlimit	ted public	release 86	126. DIS 94.	-21519
a. DISTRIBUTION / AVAILABIL Unlimited - Approv ABSTRACT (Maximum 200 v	ved for unlimit	ted public	release 8f	126. DIS 94.	-21519
a. DISTRIBUTION / AVAILABIL Unlimited – Approv ABSTRACT (Maximum 200 v	ved for unlimit	ted public	release 86	126. DIS 94.	-21519
a. DISTRIBUTION / AVAILABIL Unlimited - Approv A review of Ni A review of Ni Interfaces is made. C ii) gas, and (iii) polyn show the enhanced m idsorbed on silica, and interface can turn a r icrylate). At the poly lynamics of the interfa	WR studies done of specific interest mer interface. I lotional mobility of d swollen with to rubbery polymer mer interface, w icial layer of silar	ted public in our labor is polymens n solution we of styrene se luene. At the into a glass e show how ie coupling ag	release ratory on the adsorbed on a have used of gments of viny gas interface y one with ca the overpolymore	12b. DIS 94. 94. 94. 94. 94. 94. 94. 94. 94. 94.	f polymers adsorbed rates at the (i) solution IMR relaxation times where block copolyment how the presence of the dies of poly(<i>iso</i> -prop bismaleimide slows the
a. DISTRIBUTION / AVAILABIL Unlimited - Approv A review of Ni A review of Ni Interfaces is made. C ii) gas, and (iii) polyi show the enhanced m idsorbed on silica, and interface can turn a r incrylate). At the poly fynamics of the interfa	WR studies done (MR stu	ted public in our labor at is polymens n solution we of styrene se luene. At the into a glass e show how ie coupling ag	release ratory on the adsorbed on a have used of ments of viny gas interface y one with ca the overpolymo pent.	12b. DIS 94. 94. 94. 94. 94. 94. 94. 94. 94. 94.	f polymers adsorbed rates at the (i) solution IMR relaxation times where block copolyme how the presence of the dies of poly(<i>iso</i> -prop bismaleimide slows the
a. DISTRIBUTION / AVAILABIL Unlimited - Approv A review of Ni A review of Ni Interfaces is made. C ii) gas, and (iii) polyi show the enhanced m idsorbed on silica, and interface can turn a r incrylate). At the poly fynamics of the interfa	MR studies done of specific interes mer interface. I notional mobility of d swollen with to rubbery polymer mer interface, w icial layer of silar	ted public in our labor at is polymens n solution wo of styrene se luene. At the into a glass e show how ie coupling ag	release ratory on the adsorbed on a have used of gments of viny gas interface, y one with ca the overpolymore jent.	12b. DIS 94. 94. 94. 94. 94. 94. 94. 94. 94. 94.	f polymers adsorbed rates at the (i) solution IMR relaxation times where block copolyme how the presence of the dies of poly(<i>iso</i> -prop bismaleimide slows the
a. DISTRIBUTION / AVAILABIL Unlimited - Approv A review of Ni A review of Ni Interfaces is made. C ii) gas, and (iii) polyi show the enhanced m idsorbed on silica, and interface can turn a r icrylate). At the poly fynamics of the interfa	MR studies done of specific interes mer interface. I notional mobility of d swollen with to rubbery polymer mer interface, w icial layer of silar	ted public in our labor is polymers n solution wo of styrene se luene. At the into a glass e show how he coupling ag	release gratory on the adsorbed on a have used of gments of viny one with cather overpolyment.	94 94 dynamics o solid subst leuterium N lpyridine-sty we show i rbon-13 stu erization of	F polymers adsorbed rates at the (i) solution in the presence of the polymers adsorbed rates at the (i) solution images at the (i
a. DISTRIBUTION / AVAILABIL Unlimited - Approv A review of Ni A review of Ni Interfaces is made. Co ii) gas, and (iii) polyn show the enhanced m idsorbed on silica, and interface can turn a r icrylate). At the poly lynamics of the interfa	MR studies done of specific interest mer interface. I notional mobility of d swollen with to rubbery polymer mer interface, w icial layer of silar	in our labor is polymers n solution we of styrene se luene. At the into a glass e show how the coupling ag	release gratory on the adsorbed on a have used of gments of viny gas interface, y one with cathe overpolymorent.	12b. DIS 94. 94. 94. 94. 94. 94. 94. 94. 94. 94.	F polymers adsorbed rates at the (i) solution in the presence of the polymers and the presence of the poly (<i>iso</i> -proprise) bismale imide slows the presence of the poly (<i>iso</i> -proprise) bismale imide slows the presence of the poly (<i>iso</i> -proprise) bismale imide slows the presence of the poly (<i>iso</i> -proprise) bismale imide slows the presence of the poly (<i>iso</i> -proprise) bismale imide slows the presence of the poly (<i>iso</i> -proprise) bismale imide slows the presence of the poly (<i>iso</i> -proprise) bismale imide slows the presence of the poly (<i>iso</i> -proprise) bismale imide slows the presence of the poly (<i>iso</i> -proprise) bismale imide slows the presence of the poly (<i>iso</i> -proprise) bismale imide slows the presence of the poly (<i>iso</i> -proprise) bismale imide slows the presence of the poly (<i>iso</i> -proprise) bismale imide slows the presence of the poly (<i>iso</i> -proprise) bismale imide slows the presence of the poly (<i>iso</i> -proprise) bismale imide slows the presence of the poly (<i>iso</i> -proprise) bismale imide slows the presence of the poly (<i>iso</i> -proprise) bismale imide slows the presence of the poly (<i>iso</i> -proprise) bismale imide slows the presence of the poly (<i>iso</i> -proprise) bismale imide slows the presence of the poly (<i>iso</i> -proprise) bismale imide slows the presence of the poly (<i>iso</i> -proprise) bismale imide slows the presence of the poly (<i>iso</i> -proprise) bismale imide slows the presence of the poly (<i>iso</i> -proprise) bismale imide slows the presence of the poly (<i>iso</i> -proprise) bismale imide slows the presence of the poly (<i>iso</i> -proprise) bismale imide slows the presence of the poly (<i>iso</i> -proprise) bismale imide slows the presence of the poly (<i>iso</i> -proprise) bismale imide slows the presence of the poly (<i>iso</i> -proprise) bismale imide slows the presence of the poly (<i>iso</i> -proprise) bismale imide slows the presence of the poly (<i>iso</i> -proprise) bismale imide slows the presence of the poly (<i>iso</i> -proprise) bismale imide slows the presence of the poly (<i>iso</i> -proprise) bismale imide slows the presence of the poly (<i>iso</i> -proprise)
a. DISTRIBUTION / AVAILABIL Unlimited - Approv A review of Ni A review of Ni Interfaces is made. Co ii) gas, and (iii) polyi show the enhanced m adsorbed on silica, and interface can turn a r acrylate). At the poly dynamics of the interfa . SUBJECT TERMS Polymers, Interfa	MR studies done MR studies done of specific interes mer interface. I notional mobility of d swollen with to rubbery polymer mer interface, w icial layer of silar	in our labor is polymers n solution we of styrene se luene. At the into a glass e show how ie coupling ac	release ratory on the adsorbed on have used of gments of viny gas interface y one with ca the overpolymore jent. DTIC QUALI	12b. DIS 94. 94. 94. 94. 94. 94. 94. 94. 94. 94.	F polymers adsorbed rates at the (i) solution improvement of polymers adsorbed rates at the (i) solution improvement of the presence of the rates of poly(<i>iso</i> -proprise bismaleimide slows the dies of poly(<i>iso</i> -proprise bismaleimide slows the dies of poly(<i>iso</i> -proprise) bismaleimide slows t
a. DISTRIBUTION / AVAILABIL Unlimited - Approv A review of Ni ABSTRACT (Maximum 200 v A review of Ni Interfaces is made. C ii) gas, and (iii) polyn show the enhanced m idsorbed on silica, and nterface can turn a r icrylate). At the poly lynamics of the interfa SUBJECT TERMS Polymers, Interfa SECURITY CLASSIFICATION OF REPORT Unclassified	MR studies done of specific interes mer interface. I notional mobility of d swollen with to rubbery polymer mer interface, w icial layer of silar	in our labor is polymers n solution we of styrene se luene. At the into a glass e show how be coupling ac aces	release ratory on the adsorbed on a have used on a have used on a have used on a solution of viny a gas interface y one with ca the overpolymore jent. DTIC QUALI	94. 94. 94. 94. 94. 94. 94. 94. 95. 94. 94. 94. 94. 94. 94. 94. 94. 94. 94	Fribution CODE -21519 f polymers adsorbed rates at the (i) solution image in the figure block copolyme how the presence of the rates of poly(<i>iso</i> -proprises of poly(<i>iso</i> -proprises of poly(<i>iso</i> -proprises of the bismaleimide slows the 15. NUMBER OF PAGES 6 16. PRICE CODE 20. LIMITATION OF ABSTR

1

.....

OFFICE OF NAVAL RESEARCH

Grant N00014-91-J-1274

R&T Code 413m005---04

Technical Report # UMR-FDB-41

NMR Studies of Polymers at Interfaces

by

Frank D. Blum

Department of Chemistry and Materials Research Center University of Missouri-Rolla Rolla, MO 65401

(314) 341-4451

Prepared for Publication in

Polymeric Materials Science and Engineering

July 8, 1994

Reproduction in whole, or in part, is permitted for any purpose of the United States Government.

This document has been approved for public release and sale: its distribution is unlimited.

NMR Studies of Polymers at Interfaces

Frank D. Blum

Department of Chemistry and Materials Research Center University of Missouri-Rolla Rolla, MO 65401

INTRODUCTION

Polymers are usually used in applications with other materials as a filler, fiber or matrix. These systems may be diverse and span a broad range of applications. The ultimate properties of such systems depend not only on the bulk properties of the components, but also on how they interact. This interaction chiefly occurs through an interfacial layer between the two bulk materials. Unfortunately, the interfacial material is difficult to study because it is often so thin.

Thin films are not easy to study with macroscopic techniques, but are often reasonable to study with microscopic ones. Many of the microscopic techniques require a clear sample to probe them or their use limits analysis to the outer surface. NMR does not suffer from this limitation and can be used on opaque materials. Unfortunately, it does suffer from relatively low sensitivity. In order to cope with this low sensitivity, high surface area materials must be used.

In this paper, the results of several studies performed in our laboratory on interfacial materials using NMR techniques are discussed. Specifically, the focus is on the dynamics of interfacial species, attached to solid substrates, at the solid-liquid, solid-gas, and solid-polymer interface. The application of NMR to problems of interfacial polymers [1], thin organic films [2], and the use of NMR-active isotopes at interfaces [3] have been reviewed by the author.

EXPERIMENTAL

The spectra shown and discussed below were mostly taken on a Varian VXR-200 NMR spectrometer nominally operating at 200 MHz for protons, 50 MHz for ¹³C, and 31 MHz for ²H. The ¹³C solid spectra were taken with magic-angle spinning (MAS) and high-power proton decoupling (DD). The solid-state deuterium spectra were taken with a quadrupole echo with an alternate 180° pulses (SSECHA) and the appropriate phase cycling to reduce coherent noise. High power pulses (2µs for 90°) and fast digitization was also used. Liquids spectra and relaxation times were taken with standard equipment and pulsed techniques.

RESULTS AND DISCUSSION

In order to illustrate some of the possible applications of NMR to polymeric materials at interfaces, we examine three different situations where the adsorbates are located at different interfaces. The scope will be restricted to adsorbates on solid surfaces.

Solid-Liquid Interface

Polymers are now being designed for optimum performance as stabilizers. Block copolymers may be useful as compatabilizers or as interfacial agents. An interesting system is blocky poly(styrene-co-2vinylpyridine) (VPS) adsorbed on silica. In this system, the vinylpyridine adsorbs to silica much more strongly than styrene. In this self-assembling system, the 2-vinylpyridine (VP) segments may be considered to be terminally attached and the styrene (S) segments may be extended away from the surface.

In order to probe the dynamics of these polymers, two terpolymers were prepared [4] with deuterium atoms selectively placed on the styrene methine. They were polymerized in a blocky fashion by sequential addition with anionic polymerization. These polymers are labelled VPDSS and VPSDS where DS and S distinguish deuterostyrene from styrene, respectively.



VPDSS

VPSDS

Both polymers were polymerized to molecular weights of about $M_W = 20,000$ g/mol with polydispersities of 1.4-1.5. The values of x, y, and z were such that the polymers were 25 % VP, 37.5% DS, and 37.5% S. The polymers were adsorbed onto silica surfaces (Cab-O-Sil, grade M-5, surface area 200 m²/g) from toluene and carbontetrachloride.

¹³C NMR spectra gave a strong indication of differences between the VPS polymer in solution and that adsorbed on silica, both diluted with toluene. In the solution case, all resonances for both parts of the polymer were narrow and resolved, indicative of rapid motion of the segments. In contrast, on the surface, but swollen with toluene, only the styrene resonances were observed. The VP resonances were broadened because of their interaction, and relative immobility, with the surface. Thus the spectra were consistent with the notion of the polymer being bound through the VP segments.

Deuterium NMR relaxation times T_1 and T_2 of the backbone deuteron of the polymers have also been measured in different solvents. The liquid-like resonance was found to be adequately described by a single exponential decay constant. Some results of these measurements are found in Table I. While there are more quantitative ways to interpret the relaxation time measurements [4,5], we have found that the T_1/T_2 ratio is a good measure of the relative mobility of the polymer.

The relaxation data for the two polymers (VPDSS vs VPSDS), swollen with the same solvent, are similar in magnitude for each case. Slightly longer relaxation times are found in the VPSDS where the deuterated segments are further away from the point of attachment (VP) to the surface. In this regime, a longer relaxation time is indicative of less restricted motion. Comparison of the results for the same polymer in different solvents reveals that the relaxation times are lengthened as the solvent quality increases, also suggesting less restricted motion in good solvents. The ratios of the relaxation times shown in the table are smallest for the good solvent, toluene. Surprisingly, the ratio for the surface-bound polymers in toluene is even less than that for the polymers in solution. This is consistent with the notion that the mobility of the styrene segments on the surface, swollen in toluene, is greater than that in solution. This is at first a surprising result, but is probably due to very different segment-segment interactions in solution and in stretched out chains.

Table I. Relaxation data for VPDSS and VPSDS on silica in different solvents at 18 °C.

SYSTEM	SOLVENT	I <u>1</u> (ms)	I <u>2(ms)</u>	I <u>1</u> /I2
VPDSS	toluene	3.63	3.38	1.07
	CCI4/CH3OH	3.34	2.05	1.63
	CCl4	3.05	1.80	1.69
	toluene solution*	3.63	2.75	1.32
VPSDS	toluene	3.94	3.60	1.09
	CCI4/CH3OH	3.49	2.76	1.26
	CCl4	2.97	1.92	1.55
	toluene solution*	3.94	3.25	1.21

*interpolated to the same T1 value as for the surface/toluene system.

Thus for the surface-bound polymers the picture that emerges is one of highly extended, rapidly moving polymer segments when swollen with toluene. In the presence of the other solvents, the polymer segments maybe somewhat extended, but not as extended as in toluene. Their molecular motion is also significantly reduced compared to that in toluene. The relative mobility of the styrene segments is dependent on the solvent quality.

Solid-Gas Interface

The mobility of a polymer adsorbed on a solid surface has been probed indirectly with ¹³C NMR using magic-angle spinning and dipolar (highpower proton) decoupling. Poly(*iso*-propyl acrylate) (PiPA) was chosen for these studies because it is a flexible polymer and above its glass transition temperature under ambient conditions. Shown in Figure 1 are the MAS-DD spectra of the bulk polymer and that adsorbed at monolayer coverage on silica [6]. In bulk, the spectrum shows only the resonances from the side-chain carbonyl and methyl groups, with only a hint of the side chain methine. In contrast, the monolayer-surface spectrum shows resolved resonances for all of the carbons expected.

While it is not always possible to reproduce this startling contrast in bulk and surface species, there are some important lessons to be learned from this system. PiPA at room temperature is a flexible polymer which undergoes motion in the KHz range. This is the within frequency range of both the magic-angle spinning and also the dipolar decoupling. Incoherent motions in this frequency range can undo the coherent averaging of either the MAS or DD. On the surface, these motions are effectively slowed down and out of the operative range for MAS or DD. Consequently, the coherent averaging can take place, resulting in a resolved set of resonances. These are very similar to those obtained from a glassy polymer like poly(methyl methacrylate). It is therefore concluded that the presence of the surface has the effect of transforming the PiPA from rubbery to glassy at room temperature. From observations of the broadening as a function of surface coverage, a rough distance scale over which this interaction is effective was estimated to be about a single monolayer. The dynamics of the interfacial polymer increases as the distance away from the surface increases.



Figure 1. ¹³C MAS spectrum of PiPA in bulk (bottom) and at monolayer coverage (top) on silica.

Solid-Polymer Interface

Our work on the interface in composite materials has also shown us how to probe the interfacial species in the presence of overlayers of polymer. We have used deuterium labelling to provide the necessary contrast. Silane coupling agents which were deuterated next to the nitrogen were prepared:

These materials differed mainly in their chain length which resulted in differences in dynamics of the chains. At the silica interface, the initial monolayer is relatively rigid and as multilayers are formed, the crosslinked material becomes more flexible [7]. Ultimately, for the bulk cross-linked polymer, DABS moves about 10 times faster than the DAPS. This graded interface may be one of the reasons (in addition to chemical bonding) why these coupling agents work so well in composite materials. Shown in Figure 2 is the deuterium NMR solid-state spectrum of DABS adsorbed in monolayer coverage on silica. In the upper spectrum, the same material that has been overpolymerized with bismaleimide (BMI) is shown. The broader spectrum for the material with the polymer overlayer is indicative of (i) a change in the mechanism, and (ii) a decrease in the rate of motion of the DABS. The coupling agent becomes somewhat *locked in* with overpolymerization with BMI because of its interaction with the polymer.





CONCLUSIONS

NMR has the sensitivity to probe interfacial material on high surface area substrates. The results may be used to aid our understanding of the structural and dynamic properties of the interfacial material. These studies should be useful in their application in the design of new interfacially active species which can enhance the properties of new materials.

ACKNOWLEDGEMENT

1 4

The authors wish to thank the United States Office of Naval Research for its financial support of this project. In addition, the following researchers have worked on various parts of the work reviewed here: B. Sinha, F. Schwab, W. Meesiri, R. Funchess, H.-J. Kang, and J. Gambogi.

REFERENCES and NOTES

- 1. F.D. Blum, Colloids and Surfaces, 45, 361-376 (1990).
- 2. F.D. Blum, Annual Reviews of NMR Spectroscopy, G. Webb, ed., Academic Press, London, UK, in Press.
- 3. F.D. Blum, <u>Characterization of Composite Materials</u>, H. Ishida, ed., Manning Publications, Greenwich, CT, in Press.
- 4. F.D. Blum, B.R. Sinha, F.C. Schwab, *Macromolecules*, 23, 3592-3598 (1990).
- 5. B.R. Sinha, F.D. Blum, and F.C. Schwab, *Macromolecules*, 26, 7053-7057 (1993).
- F.D. Blum, R.B. Funchess, W. Meesiri, in <u>Solid State NMR of</u> <u>Polymers</u>, L. Mathias, Ed., Plenum Press, New York, 1991, p271-281.
- 7. H.-J. Kang and F.D. Blum, J. Phys. Chem., 95, 9391-9396 (1991).
- 8. J.E. Gambogi and F.D. Blum, *Macromolecules*, 25, 4526-4534 (1992).

Acces	sion For	
NTIS	GRA&I	0
DTIC	TAB	
Unann	ounced	
Ju sti	fication	
By	ibution/&	-
Avai	lability,	Bebe
	Avail and	/or
Dist	Special	
K I	1 1	
1		