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References and Notes

(1) Katchalsky, A.; Mazur, J.; Spitnik, P. *J. Polym. Sci.* **1957**, *23*, 513.
(2) Bloys van Treslong, C. J.; Staverman, A. J. *Recl. Trav. Chim. Pays-Bas* **1974**, *93*, 171.
(3) Lewis, E. A.; Barkley, J.; St. Pierre, T. *Macromolecules* **1981**, *14*, 546.
(4) Hughes, A. R.; St. Pierre, T. *Macromol. Synth.* **1977**, *6*.
(5) Hansen, L. D.; Lewis, E. A. *Anal. Chem.* **1971**, *43*, 1393.
(6) Hansen, L. D.; Jensen, T. E.; Mayne, S.; Eatough, D. J.; Izatt, R. M.; Christensen, J. J. *J. Chem. Thermodyn.* **1975**, *7*, 919.
(7) Parker, V. B. National Bureau of Standards, NSRDS-NBS-2; U.S. Government Printing Office: Washington, D.C., 1965.
(8) For a recent review, see: Manning, G. S. *Acc. Chem. Res.* **1979**, *12*, 443. See also ref 10–14.
(9) Fabbrizzi, L.; Micheloni, M.; Paoletti, P. *Inorg. Chem.* **1976**, *15*, 1451. (See also ref 24 and 30 for thermodynamic data on proton ionization for a large number of mono-, di-, tri-, and polyamines.)
(10) Marcus, R. A. *J. Phys. Chem.* **1954**, *58*, 621.
(11) Bloys van Treslong, C. J. *Recl. Trav. Chim. Pays-Bas* **1978**, *97*, 13.
(12) Manning, G. S. *J. Chem. Phys.* **1969**, *51*, 924; Manning, G. S. *J. Phys. Chem.* **1981**, *85*, 870.
(13) Lifson, S.; Katchalsky, A. *J. Polym. Sci.* **1954**, *13*, 43.
(14) Oloffson, G.; Zacharov, A. *Acta Chem. Scand., Ser. A* **1980**, *A34* (4), 235.
(15) Corett, R.; Bak, G. T. A. IUPAC Symposium on Macromolecules, Leiden, The Netherlands, 1970.
(16) Harned, H. G.; Owen, B. B. "The Physical Chemistry of Electrolyte Solutions", 3rd ed.; Rheinhold: New York, 1958.
(17) Tundo, P.; Venturello, P.; Angeletti, E. *Am. Chem. Soc.* **1982**, *104*, 6547.
(18) Martin, P. J.; Morss, L. R.; Strauss, U. P. *J. Phys. Chem.* **1980**, *84*, 577.
(19) Boyd, G. E. *J. Chem. Eng. Data* **1977**, *22*, 413.
(20) See ref 3, 18, 21, and 22, and *J. Poly. Sci., Polym. Symp.* **1979**, *No. 69*. "Proceedings of the 20th Prague IUPAC Microsymposium on Macromolecules"; Wiley: New York, 1979.
(21) Fenyo, J. C.; Delbin, F.; Paoletti, S.; Crescenzi, V. *J. Phys. Chem.* **1977**, *81*, 1900. Crescenzi, V.; Delbin, F.; Paoletti, S.; Skerjanc, J. *J. Phys. Chem.* **1974**, *78*, 607. Quadrifoglio, F.; Crescenzi, V.; Dolar, D.; Delbin, D. *J. Phys. Chem.* **1973**, *77*, 539.
(22) Barbucci, R.; Barone, V.; Ferruti, P.; Oliva, L. *J. Polym. Sci., Polym. Symp.* **1981**, *69*, 49. Barbucci, R.; Barone, V. *J. Solution Chem.* **1979**, *8*, 427.
(23) Everett, D. H.; Pinsent, . R. W. *Proc. R. Soc. London Ser. A* **1952**, *215A*, 416.
(24) Christensen, J. J.; Izatt, R. M.; Wrathall, D. P.; Hansen, L. D. *J. Chem. Soc. A* **1969**, 1212.
(25) Rinaldi, P. L.; Yu, C.; Levy, G. C. *Macromolecules* **1981**, *14*, 551.
(26) Tanford, C. *J. Am. Chem. Soc.* **1962**, *84*, 4240.
(27) Brandts, J. F. *J. Am. Chem. Soc.* **1964**, *86*, 4302.
(28) Benson, S. W. *J. Am. Chem. Soc.* **1958**, *80*, 5151.
(29) Tonelli, A. E. *Macromolecules* **1972**, *5*, 558. Tonelli, A. E. *Macromolecules* **1972**, *5*, 563.
(30) Christensen, J. J.; Hansen, L. D.; Izatt, R. M. "Handbook of Proton Ionization Heats"; Wiley-Interscience: New York, 1976.

Mechanisms of Polymer-Supported Catalysis. 7. Carbon-13 NMR Relaxation of Toluene in Cross-Linked Polystyrene Phase-Transfer Catalyst Gels

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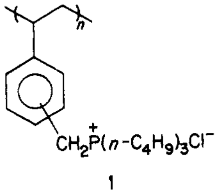
ABSTRACT: Carbon-13 spin–lattice relaxation times (T_1) and nuclear Overhauser effects have been determined for toluene in cross-linked polystyrene gel beads 16–18% ring substituted with benzyltri-*n*-butylphosphonium chloride groups. Toluene inside the beads and toluene outside the beads gave separate ^{13}C peaks for each carbon atom. The T_1 values and rate constants for exchange of toluene between the sites were measured by selective T_1 experiments with concurrent relaxation and exchange. The T_1 values of all protonated carbon atoms of toluene inside the beads were reduced to 0.05–0.33 times their values in low-viscosity toluene solutions. The T_1 values of aromatic carbon atoms of toluene outside the beads were reduced to 0.25–0.5 times their values in low-viscosity toluene solutions. The T_1 results are explained by slower rotational diffusion of toluene in the cross-linked polystyrene gels. The self-diffusion coefficient of toluene in the gel is estimated from the exchange rate constants to be 0.02 times that in liquid toluene.

In ^{13}C nuclear magnetic resonance spectra of cross-linked polystyrene gels in toluene,[1] the solvent peaks appear as doublets instead of proton-decoupled singlets. Since the NMR samples consist of toluene-swollen beads 0.1–0.3 mm in diameter immersed in toluene, the two peaks of each doublet were assigned to toluene inside the beads and toluene in the interstices. Similar doublets have been reported for organic solvents,[2,3] counterions,[2,4,5] and water[3,6–10] in ion-exchange resins. The polystyrenes in this investigation were 16–18% ring substituted with benzyltri-*n*-butylphosphonium ions (1). They have been used extensively as phase-transfer catalysts for reactions such as that of aqueous sodium cyanide with 1-bromooctane in toluene.[11–14] This paper reports the spin–lattice relaxation times of the toluene doublets in the ^{13}C NMR spectra and the rate constants for exchange between the two environments.



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NMR relaxation of small organic molecules has been studied in a variety of synthetic and naturally occurring heterogeneous systems, chiefly using ^{1}H, ^{2}H, ^{13}C, and ^{19}F nuclei.[15] The ^{13}C spin–lattice relaxation time (T_1) is particularly useful because its measurement requires no isotopic labeling and relaxation by the direct dipolar mechanism is intramolecular, allowing interpretation in

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terms of rotational correlation times. ^{13}C T_1 values for functional groups covalently attached to silica gel[16-18] and for small molecules adsorbed on silica gel,[19-22] alumina,[23] sheet silicates,[24] and zeolites[20,25-28] all are shorter than in liquids of low viscosity.

Polymer gels exhibit high-resolution ^{13}C NMR spectra when swollen by good solvents.[29-40] Both ^{13}C spin–lattice relaxation of the chains in cross-linked polystyrene gels[32,37] and ESR line width measurements of rotational diffusion of nitroxyl radicals bound to cross-linked polystyrenes[41-43] indicate substantial motion in the gels, although the mobility of the network polymer chains is less than that of the corresponding chains in polymer solutions. The degree of rotational freedom decreases with increased cross-linking and increases with increased swelling of the network. Similar results have been found in magic angle spinning ^{1}H NMR studies.[44,45] Overall rotational diffusion of water in agar[46] and of pyridine in calcium alginate[47] is slower in the gels than in low-viscosity liquids.

Experimental Section

Sample Preparation. Reagent grade toluene was used without further purification. A typical sample was prepared by placing the polymer beads[12] in an NMR tube, adding toluene, and allowing the beads to swell. Air bubbles were removed by application of a slight vacuum or centrifugation and by shaking the tube. To some samples benzene-d_6 or toluene-d_8 was added to provide the spectrometer frequency lock signal. Some of the samples containing benzene-d_6 were sealed under vacuum after degassing with three to five freeze–pump–thaw cycles. Others were only capped and contained dissolved air. In some samples the spectrometer lock signal was provided by Me$_2$SO-d_6 in a sealed 5-mm NMR tube placed concentrically in the 12-mm tube. To minimize the amount of interstitial solvent a vortex plug was inserted to the level of the polymer beads. The samples with no interstitial toluene were prepared by evaporating the toluene from a sample containing a tube of Me$_2$SO-d_6 and weighing the entire 12-mm tube before each spectral measurement to determine the net weight of toluene. With 47 wt % toluene the polymer beads appeared translucent, but with less toluene they became opaque.

Spectra. Spectra were obtained at 75.43 MHz with a Varian XL-300 instrument and at 25.2 MHz with a Varian XL-100(15) instrument equipped with a Nicolet TT-100 pulse Fourier transform accessory. At 25.2 MHz 12-mm sample tubes, a 6000-Hz frequency range, 8K data points, exponential multiplication of the FID equivalent to 0.5–1.0-Hz line broadening, and 60–200 acquisitions were used. At 75.43 MHz 5-mm sample tubes, a 6000-Hz frequency range centered 1500 Hz downfield from the toluene methyl peaks, 4K data points, 3.5-Hz line broadening, and 36–48 acquisitions were used. The sample, with a bed depth of at least 30 mm, was centered in the receiver coil of the instrument. Samples were spun at 10 Hz. Line widths were measured by TT-100 computer simulation of 400–500-Hz spectral width expansions of the methyl region of the spectra. Probe temperature at 25.2 MHz was measured with a calibrated thermometer in a 12-mm tube of toluene immediately before and after each experiment. Probe temperature at 75.43 MHz was read directly at the console of the calibrated instrument.

Spin–lattice relaxation data at 25.2 MHz were obtained by the fast inversion–recovery method using 8–16 spectra per experiment with the longest delay time between 180° and 90° pulses equal to 2–10 times (usually 4–5 times) the apparent toluene methyl group T_{1A} value. The three adjustable parameter[48] program T1IR3 with the Nicolet computer was used to measure peak heights and calculate apparent T_1 values. This procedure gave good agreement of T_1 values of a degassed solution of toluene in benzene-d_6 with the highest toluene T_1 values in the literature.

Selective inversion in the 75.43-MHz spectra was achieved with the Dante soft pulse sequence[49] for the 180° pulse of a fast inversion–recovery T_1 experiment. Details are described elsewhere.[50]

Nuclear Overhauser effects were measured from peak heights of fully decoupled and gated decoupled spectra using a 90° pulse length and a delay between acquisitions of 10 times the apparent toluene methyl T_{1A} value. In duplicate 25.2-MHz control experiments the NOE value of ethylene glycol was found to be 1.93 and 2.03, in good agreement with the theoretical value of 2.00.

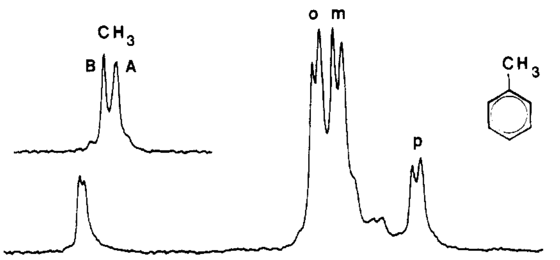
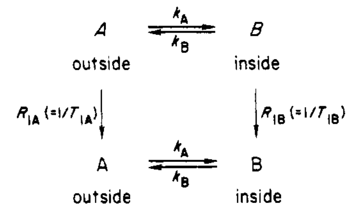


Figure 1. ^{13}C NMR spectrum of 100/200-mesh, 2% cross-linked polystyrene 1 in 3/1 toluene/benzene-d_6, degassed. The spectrum comes from an NOE experiment which used a 75-s delay between pulses. The benzene-d_6 shows larger peaks in this spectrum than in most T_1 spectra because of the long delay.

Scheme I



Computation of T_1. Details of the method are described separately.[50] A Fortran program, MT-NMR, for an IBM 7081D computer fit magnetization intensity vs. time data by Marquardt nonlinear least-squares analysis to the Bloch equations modified for chemical exchange in the format of Led and Gesmar[51] as shown in Scheme I, in which *A* and *B* are excited toluene carbon atoms and A and B are toluene carbon atoms at equlibrium magnetization, R_{1A} and R_{1B} are relaxation rate constants, T_{1A} and T_{1B} are relaxation times, and k_A and k_B are rate constants for exchange. The change in magnetization of each signal is a sum of two exponential functions which involve the rates of spin–lattice relaxation of nuclei in both environments and the rate of exchange.[51] The least-squares analysis minimizes deviations from seven adjustable parameters in a conventional T_1 data set: M_A^{∞}, M_A^0, M_B^{∞}, and M_B^0, the magnetization peak heights of signals A and B at time infinity and time zero, R_{1A} and R_{1B}, and k_A. The reverse rate constant k_B is a dependent variable calculated from $k_B = k_A\alpha\ M_A^{\infty}/M_B^{\infty}$, where α = (line width of A)/(linewidth of B). In the complementary selective inversion experiments the initial magnetization $^*M_A^0$ and $^*M_B^0$ made a total of nine adjustable parameters in the computation. First R_{1A} was fixed equal to its value in homogeneous solution, and the calculations were carried out with six or eight adjustable parameters. Then R_{1A} was set free and the calculation was repeated.

A Second Fortran program, MT-GEN, was used to generate synthetic data sets with any desired values of the above variables and any desired random errors in peak heights. Application of MT-GEN showed that typical experimental data sets had approximately 3% standard deviations of peak heights. The standard deviations of relaxation rate constants calculated with seven adjustable parameters from 25.2-MHz data were usually 5–25% of the reported value. The standard deviations in k_A and k_B from 25.2-MHz T_1 experiments were 0.3–3.0 times the calculated values and are not reported. The complementary selective inversion experiments at 75.43 MHz allowed calculation of all relaxation times and rate constants with standard deviations of 4–12%.

Results

Figure 1 shows a typical ^{13}C NMR spectrum of toluene in a 100/200-mesh (75–150 μm) polystyrene gel (1).[12] Every carbon signal appears as a doublet due to toluene inside and outside the beads. The narrower peak of each doublet at lower field (peak B) is due to toluene inside the beads. The assignment is based on reduction in peak area and eventual disappearance of peak A as solvent is removed from the interstices and on the longer spin–lattice

Table I
Effects of Removal of Toluene from Interstices and Partial Evaporation of Toluene from Beads[a]

wt % toluene	line width,[b] Hz		app T_{1B}, s			η[c]	
	CH_3	*o,m*	CH_3	*o,m*	*p*	CH_3	*o,m,p*
50[d]	17	34	5.6	3.4	2.4	1.4	1.4
47[e]	25	45	5.4	3.1	2.3	0.9	1.1
42[f]	30	49	5.5	2.5	2.1	0.9	1.1
17[f]	36	55	3.8	1.68	1.23	0.8	1.2
7[e,g]	52	67	2.1	0.64	0.55	0.8	0.9

[a] 100/200-Mesh beads, 2% cross-linked, 30 °C, 25.2 MHz. [b] Combined width of all peaks in multiplet when peaks are resolved or of one broad peak when not resolved. [c] Determined from peak heights of signal B or of broad peak from combined signals A and B when peaks are not resolved. [d] Calculated from swelling ratio. These data are for beads with interstitial toluene and are averages from three to five experiments. [e] One experiment. [f] Average of two experiments. [g] Toluene content estimated from spectral signal to noise, line width, and number of acquisitions.

relaxation time of peak A than of peak B ($T_{1A} > T_{1B}$). In a large number of experiments with 2% cross-linked, 60/100- and 100/200-mesh particles at 30 °C the methyl carbon line widths at 25.2 MHz ranged from 3.5 to 8.0 Hz, and the ratio of the line widths (α) ranged from 1.25 to 1.91. At 75.43 MHz methyl carbon line widths were 16–42 Hz and α was 1.86–2.20. Separations between the methyl peak maxima were 10–12 Hz at 25.2 MHz and 23–36 Hz at 75.43 MHz.

"Apparent" spin–lattice relaxation times were calculated from conventional inversion–recovery T_1 data for every resolved protonated carbon signal of toluene by fitting the data to a single-exponential function. The data also were used to calculate "real" T_1 values which take into account exchange of toluene between the beads and the interstices according to Scheme I, as described in the Experimental Section. Selective inversion T_1 experiments at 75.43 MHz were carried out only on the toluene methyl carbon signals.

One sample was studied from −31 to +74 °C at 25.2 MHz. Over the entire range there was no apparent change in the line width of the methyl peak A (random variation from 5.5 to 8.0 Hz). The methyl peak B due to intraparticle toluene decreased markedly in relative area from +14 to −31 °C, and its width could not be measured. The separation between the methyl carbon peak maxima was invariant (10.5–11.5 Hz) from +1 to +74 °C. From +1 to −31 °C the area of methyl peak B decreased from 42% to 25% of the total methyl signal area. At +1 and −31 °C the aromatic carbon doublets were no longer resolved. Apparent T_{1A} and T_{1B} values of every signal increased as the temperature increased from +1 to +74 °C and became nearly equal at 74 °C, as shown in Figure 2.

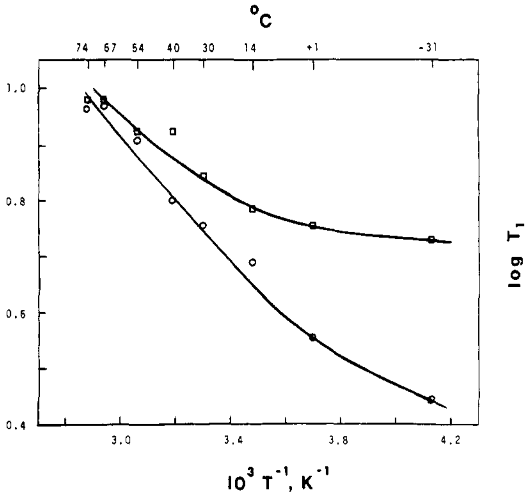


Figure 2. Temperature dependence of apparent methyl carbon relaxation times T_{1A} (□) and T_{1B} (○) of toluene in 2% cross-linked 100/200-mesh beads. The 30 °C data points are averages of five experiments. All other data points are single experiments.

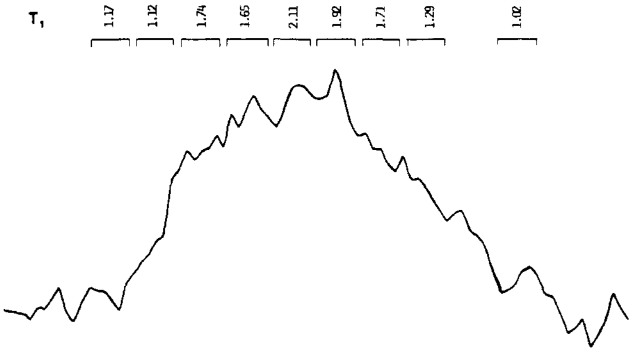


Figure 3. T_1 values of the toluene methyl carbon in a gel dried to 7% toluene determined at various frequencies across the broad peak. (See Table I.) Data used in each calculation were maxima or minima of signal intensities within a range of five spectral data points.

Removal of the interstitial toluene and evaporation of the toluene from the beads caused disappearance of the upfield half of each doublet and severe broadening of the remaining signal as shown in Table I. T_{1B} also decreased as the toluene content of the beads decreased. With the broadest methyl signal in a bead sample containing only 7% toluene by weight, the apparent T_{1B} values calculated from signal intensities at various positions across the broad peak decreased from the center to the edges. (See Figure 3.)

Table II summarizes real T_1 and exchange rate constant data at ambient temperature. In accord with Scheme I

Table II
Spin–Lattice Relaxation Times (s) and Exchange Rate Constants (s^{-1})[a]

		T_{1A} fixed[b]			T_{1A} variable			
carbon	freq, MHz	T_{1B}	k_A	k_B	T_{1A}	T_{1B}	k_A	k_B
			60/100-Mesh Beads					
CH_3	25.2	3.2			10.2	3.8		
o,m	25.2	1.63			7.4	2.3		
p	25.2	1.01			6.1	1.42		
CH_3	75.43	5.3	0.25	0.42	13.4	6.2	0.22	0.37
			100/200-Mesh Beads					
CH_3	25.2	3.3			9.0	4.7		
o,m	25.2				6.5	2.4		
p	25.2				4.1	1.82		
CH_3[c]	75.43	5.0	0.42	0.69	12.8	6.0	0.39	0.62

[a] Each value is an average from three to five experiments; 25.2 MHz at 30 °C; 75.43 MHz at 23 °C. [b] T_{1A} at 25.2 MHz was fixed to values for degassed toluene/benzene-d_6 in Table IV. T_{1A} of CH_3 at 75.43 MHz was fixed to 15.0 s. [c] 150/200 mesh.

Table III
Nuclear Overhauser Effects (η) on Toluene ^{13}C Peaks[a]

sample	freq, MHz	CH_3(A)	CH_3(B)	*o,m*(A)	*o,m*(B)	*p*(A)	*p*(B)
100/200 mesh[b]	25.2	1.1	1.2	1.2	1.2	1.5	1.3
60/100 mesh	25.2	0.9	1.0	1.0	1.0	1.3	1.1
partly dried[c]	25.2		0.9		1.1		1.1
toluene/C_6D_6[d]	25.2	0.54		1.80		1.89	
60/100 mesh[b]	75.43	0.77	0.80	0.95[e]		1.05[e]	

[a] η = (peak height with full ^{1}H decoupling)/(peak height with decoupler gated off during delay) − 1. A = toluene outside beads. B = toluene inside beads. *o,m* data are average values; 25.2 MHz at 30 °C; 75.43 MHz at 23 °C. [b] Average of two experiments. [c] 42 wt % toluene. See Table I. [d] Literature values for solutions are as follows: CH_3 0.61, *o,m* 1.4–1.73, *p* 1.3–1.74 (at 38 °C)[60]; *o,m* 1.55–2.0, *p* 1.6–1.85 (at 23 °C)[61]. [e] Peaks not resolved.

Table IV
T_1 Values (s) of Toluene in Solutions

		this work[a]		lit.,[60] 38 °C	
carbon	freq, MHz	degassed[b]	undegassed	degassed	undegassed
CH_3	25.2	16.1	13.3[c]		16.3
o,m	25.2	23.6	16.0[c]	24	20.5
p	25.2	18.8	13.1[c]	18	15
CH_3	75.43	15.6	14.2[b]		

[a] 25.2 MHz at 30 °C; 75.43 MHz at 23 °C. [b] 15 wt % benzene-d_6. [c] At 25.2 MHz with a 10% solution of poly(styrene-*co*-(chloromethyl)styrene), 75 wt % styrene in copolymer.

magnetization intensities as a function of time were treated as sums of two exponential functions by the Bloch equations modified for chemical exchange.[49-59] For 25.2-MHz experiments samples were prepared with and without dissolved oxygen, with benzene-d_6 internal reference and with Me_2SO-d_6 external reference, with a vortex plug packing the sample, and with excess solvent in the tube. None of these variables affected the T_1 values outside of experimental error. For 75.43-MHz experiments samples were prepared with either benzene-d_6 or toluene-d_8 as internal reference, and no significant effects of reference solvent on the T_1 values or exchange rate constants were observed.

Nuclear Overhauser effects (η) and T_1 were determined for toluene solutions (Tables III and IV). One possible cause of reduced T_1 and η values in the heterogeneous samples is paramagnetic impurities. ESR experiments on two typical polymer bead samples in toluene revealed no detectable signal, which corresponds with upper limits of 10^{15} free spins in the ESR sample and 1.7 μM of paramagnetic species in the NMR samples. From data on the effect of $Cr(acac)_3$ on T_1 values,[62,63] 9.0 mM $Cr(acac)_3$ would be required in the polymer beads to cause the observed reduction in T_1 of ortho and meta carbons of toluene from solution values to those observed in the polymer beads. Although a different paramagnetic species would not have exactly the same effect as $Cr(acac)_3$ on T_1, the absence of detectable free spins in the beads makes it highly unlikely that the lower T_1 and η values both inside and outside of the beads are due mainly to relaxation by paramagnetic impurities.

The component of T_1 due to direct dipolar relaxation (T_1(DD)) is inversely related to the correlation time for rotational diffusion. Comparions of T_1(DD) values in bead samples and in toluene solution are in Table V.

Discussion

The T_1 values of all toluene carbon atoms inside the gel polymer beads are 0.33–0.05 times the T_1 values in toluene solutions. The ^{13}C T_1 values of toluene in the interstitial liquid also are consistently lower than in toluene solutions, by factors of 2–4 for the aromatic carbons. (Compare T_{1A} values in Table II with those in Table IV.)

Table V
T_1(DD) (s) of Toluene Carbons[a]

		T_{1A} fixed[b]	T_{1A} variable[c]		liquid[d]
carbon	freq, MHz	T_{1B}	T_{1A}	T_{1B}	T_1
		60/100 mesh			
CH_3	25.2	5.8	20.3	6.9	59
o,m	25.2	2.9	12.3	4.2	26
p	25.2	1.7	8.7	2.4	19.9
CH_3	75.43	13.3	35	15.5	
		100/200 mesh			
CH_3	25.2	6.0	17.9	8.5	59
o,m	25.2		10.8	4.3	26
p	25.2		5.8	3.0	19.9
CH_3[e]	75.43	12.5	33	15.0	

[a] Calculated from $T_1(DD) = 2T_1/\eta$. [b] T_{1A} fixed to value for degassed liquid toluene. [c] See Table II. [d] Degassed. See Table IV. [e] 150/200 mesh.

Protonated aromatic ^{13}C nuclei in degassed toluene solutions undergo spin–lattice relaxation primarily by the direct dipolar mechanism with a small contribution from spin rotation. The methyl carbon relaxes with a greater contribution from spin rotation. The reductions in all T_1 values in the polymer bead samples suggest that rotational diffusion of toluene is slower both inside and outside the gel beads in toluene solutions. The increases in T_1 for all carbon atoms as temperature increases (Figure 2) indicate that spin rotation is not the primary relaxation mechanism, because spin rotation relaxation causes T_1 to decrease as temperature increases.

The case for dominant direct dipolar relaxation is not so clear when one examines the nuclear Overhauser effect (η) values. The increased η at 25.2 MHz of the methyl carbon both inside and outside the beads compared with toluene solutions indicates greater direct dipolar and less spin rotation contribution to methyl carbon relaxation. However, none of the η values approach the theoretical limit of 2.0 for direct dipolar relaxation only under the extreme narrowing condition, $\omega_0\tau_c \ll 1$, in which ω_0 is the spectrometer frequency and τ_c is the rotational correlation time. Major contributions to relaxation by interaction with dissolved oxygen or other paramagnetic impurities can be ruled out, and the spin rotation contribution should be smaller inside the beads because of slower molecular motion. More likely, relaxation of the toluene aromatic carbons both inside and outside the beads occurs mainly by the dipolar mechanism, and a small fraction of the toluene molecules lie in an environment in which motion is highly restricted. Rotational correlation times in the restricted environment must be much longer than in the extreme narrowing limit to account for the reduced η values. Diffusion in and out of such an environment should be very fast compared with the time required for detection by NMR. The fraction of molecules with restricted motion must be very small to account for observed

T_1 values of 1 s or more. Consequently the signals in the spectra should not be broadened markedly.

Reduced T_1 values in incompletely swollen beads (Table I) support a distribution of rotational correlation times of toluene inside the gel beads. The T_1 values at different frequencies of the broad toluene methyl peak in Figure 3 indicate that the toluene molecules which contribute most to the breadth of the peak have shorter relaxation times that the toluene molecules that contribute primarily to the center of the peak.

Considering both possible explanations of the low η values, limits may be placed on the factors by which rotational correlation times (τ_c) are increased in the gel samples. If relaxation occurs entirely by the direct dipolar mechanism, comparisons of the T_1 values in Table II with direct dipolar T_1 values for toluene in the absence of polymer beads in Table V show increases in τ_c by factors of about 3–20. If the reduced η values are due to some unidentified relaxation mechanism, direct dipolar contributions to T_1 can be calculated from $T_1(\mathrm{DD}) = 2T_1/\eta$. Comparisons of the T_1(DD) values in gels with those in toluene solutions in Table V show that the relaxation times inside the gel particles, T_{1B}, are shorter by factors of 6–12, and the relaxation times outside the gel particles, T_{1A}, are shorter by factors of 2.1–3.3 than in toluene solutions.

Previous NMR relaxation studies of ion-exchange resins found shorter T_1 values for water protons and for ^{13}C counterions inside the beads than for the same species in bulk water,[4-6] but in no case was the relaxation time of the interstitial species reported. Values of proton and deuteron T_1 and T_2 of water in a 10% agar gel were explained by two distinct correlation times differing by a factor >100, with less than 1% of the water molecules in the restricted environment.[46] Pyridine carbon atoms in a calcium alginate gel had T_1 values 0.19–0.36 times as long as in a 1 M solution in D_2O.[47] The η values were 0.7–0.9 in the gel compared with 1.4–1.6 in solution.[47]

Coverage of a monolayer or less of small molecules on silica gel surface or in a sheet silicate or inclusion of small molecules in zeolites increases rotational correlation times to greater than the ^{13}C NMR extreme narrowing limit.[19-28]

One other example of different relaxation times inside and outside of particles is that of ^{31}P of inorganic phosphate inside and outside of rat liver mitochondria.[65] The inside and outside ^{31}P relaxation times T_i were 0.6 and 25 s, and the exchange lifetimes were 5–20 min.

The rate constants for exchange of toluene in and out of the polymer beads could be determined with reasonable accuracy only from the 75.43-MHz selective inversion data. The rate constants are comparable with the rates of spin–lattice relaxation. If the rate constant for approach to equilibrium is limited by toluene diffusion in the gel phase, the diffusion coefficients (D_s) calculated from the rate constants and the particle radii[66] are about 6×10^{-7} cm^2 s^{-1}, compared with a likely value of $D_s = 3 \times 10^{-5}$ cm^2 s^{-1} for liquid toluene at 25 °C.[67] The rate constants determined here set an extreme upper limit for the rate of exchange of toluene in and out of catalyst 1 in a phase-transfer catalysis experiment.[11-14] The beads in the NMR experiment were tightly packed, while in a typical phase-transfer catalysis experiment the beads occupy less than 1% of the reaction mixture. The D_s of toluene in the catalyst is somewhat greater than an estimated $D_s = 1.3 \times 10^{-7}$ cm^2 s^{-1} for intraparticle diffusion of 1-bromooctane that was calculated from kinetic data for reaction of 1-bromooctane in toluene with aqueous sodium cyanide using the same catalyst 1.[68]

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References and Notes

(1) Ford, W. T. *J. Polym. Sci., Polym. Chem. Ed.* **1984**, *22*, 509.
(2) Gordon, J. E. *J. Phys. Chem.* **1962**, *66*, 1150.
(3) Doskocilova, D.; Schneider, B. *Macromolecules* **1972**, *5*, 125.
(4) Smith, W. B.; Strom, E. T.; Woessner, D. E. *J. Magn. Reson.* **1982**, *46*, 172.
(5) Sternlicht, H.; Kenyon, G. L.; Packer, E. L.; Sinclair, J. *J. Am. Chem. Soc.* **1971**, *93*, 199.
(6) Creekmore, R. W.; Reilley, C. N. *Anal. Chem.* **1970**, *42*, 570.
(7) Creekmore, R. W.; Reilley, C. N. *Anal. Chem.* **1970**, *42*, 725.
(8) Frankel, L. S. *J. Phys. Chem.* **1971**, *75*, 1211.
(9) Frankel, L. S. *Anal. Chem.* **1971**, *43*, 1506.
(10) Narebska, A.; Streich, W. *Colloid Polym. Sci.* **1980**, *258*, 379.
(11) Tomoi, M.; Ford, W. T. *J. Am. Chem. Soc.* **1980**, *102*, 7140.
(12) Tomoi, M.; Ford, W. T. *J. Am. Chem. Soc.* **1981**, *103*, 3821.
(13) Tomoi, M.; Ford, W. T. *J. Am. Chem. Soc.* **1981**, *103*, 3828.
(14) Ford, W. T.; Lee, J.; Tomoi, M. *Macromolecules* **1982**, *15*, 1246.
(15) Fraissard, J. P.; Resing, H. A., Eds. "Magnetic Resonance in Colloid and Interface Science"; D. Reidel Publishing Co.: Dordrecht, Holland, 1979.
(16) Tanaka, K.; Shinoda, S.; Saito, Y. *Chem. Lett.* **1979**, 179.
(17) Chiang, C.-H.; Liu, N.-I.; Koenig, J. L. *J. Colloid Interface Sci.* **1982**, *86*, 26.
(18) Shinoda, S.; Saito, Y. *J. Colloid Interface Sci.* **1982**, *89*, 293.
(19) Gay, I. D. *J. Phys. Chem.* **1974**, *78*, 38.
(20) Denney, D.; Mastikhin, V. M.; Namba, S.; Turkevich, J. *J. Phys. Chem.* **1978**, *82*, 1752.
(21) Takasugi, M.; Watanabe, N.; Niki, E. *Nippon Kagaku Kaishi* **1981**, 962; *Bunseki Kagaku* **1981**, *30*, 504.
(22) Resing, H. A.; Slotfeldt-Ellingsen, D.; Garroway, A. N.; Weber, D. C.; Pinnavaia, T. J.; Unger, K., p 239 in ref 15.
(23) Dawson, W. H.; Kaiser, S. W.; Ellis, P. D.; Inners, R. R. *J. Am. Chem. Soc.* **1981**, *103*, 6780.
(24) Fyfe, C. A.; Thomas, J. M; Lyerla, J. R. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 96.
(25) Sefcik, M. D. *J. Am. Chem. Soc.* **1979**, *101*, 2164.
(26) Nagy, J. B.; Guelton, M.; Derouane, E. G., p 583 in ref 15.
(27) Michel, D.; Pfeifer, H.; Delmau, J. *J. Magn. Reson.* **1981**, *45*, 30.
(28) Nagy, J. B.; Derouane, E. G.; Resing, H. A.; Miller, G. R. *J. Phys. Chem.* **1983**, *87*, 833.
(29) Schaefer, J. *Macromolecules* **1971**, *4*, 110.
(30) Yokota, K.; Abe, A.; Hosaka, S.; Sakai, I.; Saito, H. *Macromolecules* **1978**, *11*, 95.
(31) Torchia, D. A.; VanderHart, D. L. *Top. Carbon-13 NMR Spectrosc.* **1979**, *3*, 325 and references therein.
(32) Doskocilova, D.; Schneider, B.; Jakes, J. *J. Magn. Reson.* **1978**, *29*, 79.
(33) Spevacek, J.; Dusek, K. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *18*, 2027.
(34) Hodgkin, J. H.; Willing, R. I.; Eibl, R. *J. Polym. Sci., Polym. Chem. Ed.* **1981**, *19*, 1239.
(35) Manatt, S. L.; Horowitz, D.; Horowitz, R.; Pinnell, R. P. *Anal. Chem.* **1980**, *52*, 1529.
(36) Ohtani, N.; Wilkie, C. A.; Nigam, A.; Regen, S. L. *Macromolecules* **1981**, *14*, 516.
(37) Ford, W. T.; Balakrishnan, T. *Macromolecules* **1981**, *14*, 284.
(38) Jones, A. J.; Leznoff, C. C.; Svirskaya, P. I. *Org. Magn. Reson.* **1982**, *18*, 236.
(39) Live, D.; Kent, S. B. H. *ACS Symp. Ser.* **1982**, *No. 193*, 501.
(40) Nicolaisen, F. M.; Meyland, I.; Schaumburg, K. *Acta Chem. Scand., Ser. B* **1980** *B34*, 579.
(41) Regen, S. L. *J. Am. Chem. Soc.* **1974**, *96*, 5275; *Macromolecules* **1975**, *8*, 689.
(42) Veksli, Z.; Miller, W. G. *Macromolecules* **1975**, *8*, 248.
(43) Veksli, Z.; Miller, W. G.; Thomas, E. L. *J. Polym. Sci., Polym. Symp.* **1976**, *No. 54*, 299.
(44) Doskocilova, D.; Schneider, B. *Pure Appl. Chem.* **1982**, *54*, 575.
(45) Doskocilova, D.; Schneider, B.; Jakes, J. *Polymer* **1980**, *21*, 1185.
(46) Woessner, D. E.; Snowden, B. S., Jr. *J. Colloid Interface Sci.* **1970**, *34*, 290.
(47) Hall, L. D.; Yalpani, M. *Org. Magn. Reson.* **1981**, *16*, 60.
(48) Kowalewski, J.; Levy, G. C.; Johnson, L. F.; Palmer, L. *J. Magn. Reson.* **1977**, *26*, 533.
(49) Morris, G. A.; Freeman, R. *J. Magn. Reson.* **1978**, *29*, 433.
(50) Ford, W. T.; Periyasamy, M.; Spivey, H. O.; Chandler, J. P., submitted for publication.
(51) Led, J. J.; Gesmar, H. *J. Magn. Reson.* **1982**, *49*, 444.

(52) Lambert, J. B.; Keepers, J. W. *J. Magn. Reson.* **1980**, *38*, 233.
(53) Dahlquist, F. W.; Longmuir, K. J.; Du Vernet, R. B. *J. Magn. Reson.* **1975**, *17*, 406.
(54) Alger, J. R.; Prestegard, J. H. *J. Magn. Reson.* **1977**, *27*, 137.
(55) Campbell, I. D.; Dobson, C. M.; Ratcliffe, R. G.; Williams, R. J. P. *J. Magn. Reson.* **1978**, *29*, 397.
(56) Lambert, J. B.; Nienhuis, R. J.; Keepers, J. W. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 487.
(57) Baine, P.; Gerig, J. T.; Stock, A. D. *Org. Magn. Reson.* **1981**, *17*, 41.
(58) Hennig, J.; Limbach, H. H. *J. Magn. Reson.* **1982**, *49*, 322.
(59) Schotland, J.; Leigh, J. S. *J. Magn. Reson.* **1983**, *51*, 48.
(60) Levy, G. C.; Cargioli, J. D.; Anet, F. A. L. *J. Am. Chem. Soc.* **1973**, *95*, 1527.
(61) Bauer, D. R.; Alms, G. R.; Brauman, J. I.; Pecora, R. *J. Chem. Phys.* **1974**, *61*, 2255.
(62) Hexem, J. G.; Edlund, U.; Levy, G. C. *J. Chem. Phys.* **1976**, *64*, 936.
(63) Levy, G. C.; Edlund, U.; Holloway, C. E. *J. Magn. Reson.* **1976**, *24*, 375.
(64) Toluene should be treated as an asymmetric top, and rotational correlation times should be referred to the three principal axes of rotation. The data here are insufficient for such calculations. In this discussion rotational correlation time refers to an average value for toluene that is inversely proportional to T_1 in the extreme narrowing limit.
(65) Ogawa, S.; Boens, C. C.; Lee, T.-M. *Arch. Biochem. Biophys.* **1981**, *210*, 740.
(66) Helfferich, F. "Ion Exchange"; McGraw-Hill: New York, 1962; pp 259–265.
(67) Approximately equal values of D_s for toluene and benzene are assumed. This is a greater reduction in D_s in the gel phase here than in 0.5 volume fraction benzene in polystyrene: Kosfeld, R.; Zumkley, L. *Ber. Bunsenges. Phys. Chem.* **1979**, *83*, 392.
(68) Marconi, P. F.; Ford, W. T. *J. Catal.* **1983**, *83*, 160.

Mesophase Formation and Polymer Compatibility. 2. Cellulose Acetate/(Hydroxypropyl)cellulose/Diluent System

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ABSTRACT: The phase diagram of the system cellulose acetate (CA)/(hydroxypropyl)cellulose (HPC)/*N*,*N*-dimethylacetamide (DMAc) at 20 °C was investigated. The CA and HPC samples chosen have similar size and semirigid conformation composed, respectively, of ~14 and ~12 Kuhn statistical segments ~140 Å long. The binary systems CA/DMAc and HPC/DMAc exhibit a cholesteric mesophase above polymer volume fractions $v_2' \sim 0.33$ and $v_3' \sim 0.35$, respectively. Ternary systems exhibit a single isotropic phase only when the combined volume fraction is below ~0.05. When $(v_2 + v_3)$ is between ~0.1 and ~0.35, two isotropic phases exist, one containing prevalently CA and the other HPC. This incompatibility in the isotropic phase is in line with an evaluation of enthalpy parameters for the CA/HPC pair. Above the critical volume fraction, there is a composition range, which roughly corresponds to the biphasic gap of the corresponding binary systems, in which *three* phases coexist. The volume fraction of the anisotropic phase of HPC increases at the expense of the isotropic HPC phase in the presence of the anisotropic phase of CA. All compositions are invariant until all isotropic phases disappear. Henceforth, two anisotropic phases are stable, each containing pure polymer. It appears that compatibility between polymers forming similar mesophases may not be often observed, in contrast to the case of low molecular weight liquid crystals.

In a previous paper[1] we discussed the phase behavior of ternary systems composed of a rodlike polymer, a flexible polymer, and a solvent. The systems were poly(*p*-benzamide) (PBA)/polyterephthalamide of *p*-aminobenzhydrazide (X-500)/*N*,*N*-dimethylacetamide (DMAc) + 3% LiCl, and PBA/poly(acrylonitrile) (PAN)/DMAc + 3% LiCl. The results showed complete exclusion of the flexible coils from the mesophase formed by the rodlike solute. An analysis of the role of polymer compatibility, as conventionally defined by enthalpy parameters in the case of an isotropic mixture of two random coiled polymers,[2] was performed. The results showed that no demixing should have been expected for the PBA/X-500/DMAc + 3% LiCl and for the PBA/PAN/DMAc + 3% LiCl systems in the composition range investigated. Thus, in line with theoretical prediction,[3] the exclusion of the flexible polymer from the mesophase is an entropy effect related to the interference of random coils with the mutual orientation of rodlike molecules.

Rodlike molecules, able to form mesophases in binary polymer/solvent systems, should not exhibit the latter type of repulsive interference when suitably dissolved in ternary systems. Indeed, theory[4] predicts that two rodlike polymers having different axial ratios, and not necessarily the same chemical composition, should form a single anisotropic phase at sufficiently high concentration. The expectation concerning chemically different polymers is apparently verified by the not too extensive data reported in the literature.[5,6] Indeed, in the case of low molecular weight liquid crystals, the well-known compatibility rule between mesogens forming similar mesophases is used as a test for mesophase identification.[7] Lack of miscibility between low molecular weight mesogens forming similar mesophases has also been observed, but it is the exception rather than the rule. Gross differences in chemical constitution, resulting in large unfavorable mixing enthalpies, may be advocated in the latter cases.

In the case of two mesogenic polymers, the expected compatibility of the mesophases may, however, not be observed on account of the poor compatibility generally exhibited by polymers in isotropic phases and of differences in the conformation of the mesogens. In the present paper we investigate the role of compatibility in the isotropic phase for two polymers exhibiting similar conformations. The two polymers are cellulose acetate (CA) and (hydroxypropyl)cellulose (HPC) dissolved in DMAc. It will be shown that CA and HPC are not compatible in both isotropic and anisotropic solutions, giving rise to situations involving *three* coexisting phases which have not yet been theoretically predicted.