Missouri University of Science and Technology
Scholars' Mine

Opportunities for Undergraduate Research Experience Program (OURE)

Student Research & Creative Works

28 Mar 2007

Polymer Gels: Mimickin g Biological Environments

Joshua Carey

Follow this and additional works at: https://scholarsmine.mst.edu/oure

 Part of the Chemistry Commons

Recommended Citation

Carey, Joshua, "Polymer Gels: Mimickin g Biological Environments" (2007). *Opportunities for Undergraduate Research Experience Program (OURE)*. 195.
https://scholarsmine.mst.edu/oure/195

This Presentation is brought to you for free and open access by Scholars' Mine. It has been accepted for inclusion in Opportunities for Undergraduate Research Experience Program (OURE) by an authorized administrator of Scholars' Mine. This work is protected by U. S. Copyright Law. Unauthorized use including reproduction for redistribution requires the permission of the copyright holder. For more information, please contact scholarsmine@mst.edu.

Polymer Gels: Mimicking Biological Environments

OURE – 2006-2007

Chemistry Department

Date: 3-28-07

Advisor: Dr. Tadashi Tokuhiro

Student: Joshua Carey

Abstract:

A comparison of the hydrolysis of pyruvic acid in polymer gels and in aqueous environment will be studied using NMR techniques. Relaxation time and diffusion rates will be determined and compared to show the mimicking capability of the polymer gels to that of biological environments. This will allow for a means in which chemical reactions can be performed in a medium that more closely resembles the rate that the reaction would occur in biological systems.

Introduction:

Polymer gels are composed of a polymer network and a solvent. The polymer network is a solid at room temperature while the solvent is a liquid. When the polymer network and solvent are combined, a polymer gel phase is formed which is a mixture of the original phase states of the two components. It has been shown that the solvent molecules in the polymer gel acts as a complex fluid in which the solvent molecules move significantly slower than motion of the solvent molecules if no polymer network was present. This is found to be the same phenomenon that occurs in biological systems, in which the motion of water molecules in tissues is significantly slower as compared to water alone. This allows for a means in which chemical reactions can take place in an environment much closer to tissues than commonly used aqueous solutions since the polymer gels closely mimic the solvent motion that is found in tissue.

For the experiment, the reaction of the hydrolysis of pyruvic acid will be explored. The chemical reaction is as follows:

$$CH_3COCOOH + H_2O \leftarrow \rightarrow CH_3C(OH)_2COOH$$

This reversible reaction will be monitored with NMR techniques in which the peak intensities and relaxation times will be determined. This will be accomplished by taking measurements at varied temperatures of 30 ^{o}C, 32 ^{o}C, and 37 ^{o}C.

Experimental:

First a polymer network was created using a mixture of acrylamide and N-isopropyl-acrylamide. The thermal sensitivity and motion of the water as a complex fluid in the polymer gel was dependent on the ratio of these two components. The ratio of the two components used in the formation of the polymer network was chosen in such a way that the relaxation time and diffusion rate was of that of biological tissues at a temperature of 37 C which corresponds to normal body temperature.

The gels were prepared using a common technique free-radical polymerization. The ration of the two components was 668 mM N-isopropyl-acrylamide (NIPA) and 32 mM sodium acrylamide (NaAc). A cross-linking agent was also introduced to form a polymer network matrix. The cross-linking agent used was N,N'-methylethylenediamine (BIS) in which a concentration of 8.6 mM was used. The free-radical polymerization was carried out at 5 C and initiated with ammonium persulfate and accelerated with tetramethylethylenediamine. The reaction was allowed to proceed for approximately one day to ensure complete complexing. The water and moisture was then removed from the newly formed polymer complex by a freeze-drying technique in which the sample is lyophilized for about 36 hours.

The pyruvic acid used for this experiment was purified using a freeze separation process. A volume of pyruvic acid was added to a conical glass container. This conical container was then secured to a clamp positioned above a cooled water tank. The water tank was kept at a temperature of 0 C. The conical container was then slowly lowered into the water tank. After a period of time the pyruvic acid began to solidify in the bottom of the container. The liquid portion was then discarded and the solid portion allowed to become liquid again. The purified sample was then sealed and placed in a refrigeration unit to be stored for later.

The NMR tubes were prepared with samples under a vacuum system in such a way that air was removed that contained oxygen and replaced with nitrogen gas. First the 10.74 mM pyruvic acid in D2O was placed in a NMR tube and the tube attached to the apparatus. Oxygen free nitrogen gas was then introduced into the system to remove any air from the system. This was done at one atm pressure and at room temperature for a period of 30 minutes. The pressure was then reduced slightly, to approximately 700 mm Hg to seal off the NMR tube. The sample was then stored in a refrigeration unit to be stored for NMR analysis.

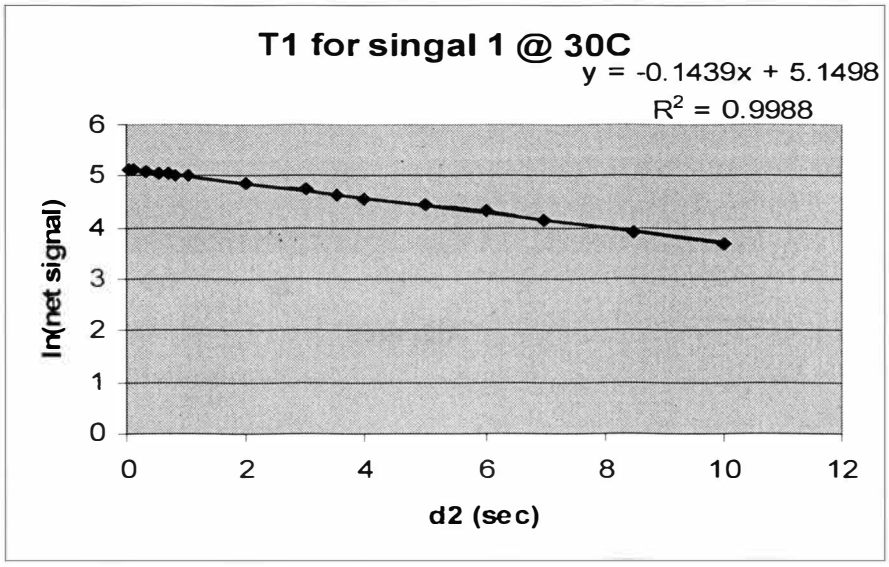
The NMR tube containing the sample of the polymer network and the pyruvic acid sample was prepared in a similar fashion. First, a small piece of the polymer network was massed and placed carefully at the bottom of the NMR tube. Next, 10.74 mM pyruvic acid in D2O was added to the sample in such a ratio that no excess solvent was present at the temperatures the samples would be analyzed. The sample was then thoroughly degassed using a freeze-pump-thaw process for eight cycles. The sample was then flushed and sealed using the same process as for the sample of pyruvic acid only.

The NMR used for this experiment was a Varian ENOVA-UNITY high resolution spectroscopy that operates at 400 MHz. The proton resonance was set at 399.793 MHz. The optimum 90 degree pulse width was found to be 10.3 microseconds. Relaxation time inversion recovery method was used to determine the relaxation time of the pyruvic acid in the isolated sample, while the null recovery method was used to determine the relaxation time of the pyruvic acid in the sample with the polymer network.

Data:

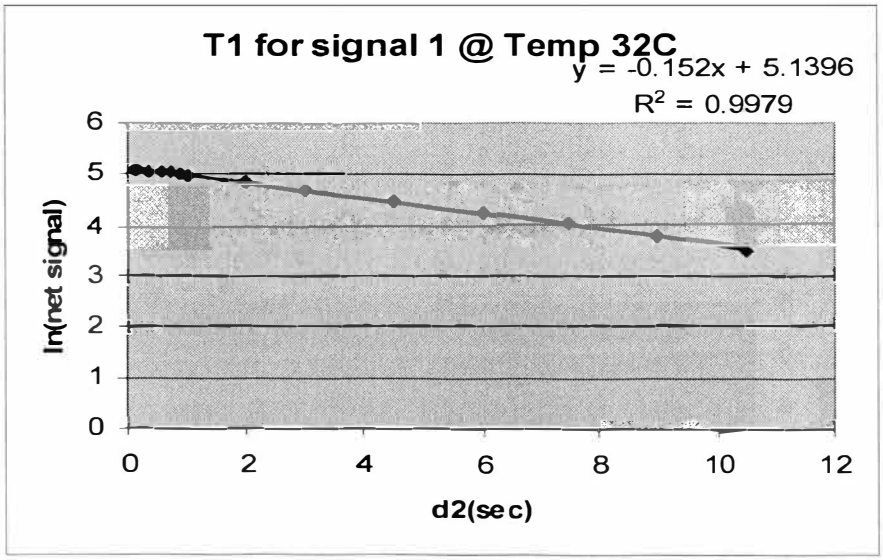
1. Pyruvic acid – No polymer network present – Temperature @ 30 C

d2 (sec)	peak height	Δ signal	ln(Δ signal)
0.05	-85	170	5.1358
0.1	-84.5	169.5	5.1329
0.3	-79.5	164.5	5.1029
0.5	-74	159	5.0689
0.65	-72	157	5.0562
0.8	-68	153	5.0304
1	-63	148	4.9972
2	-45	130	4.8675
3	-29	114	4.7362
3.5	-19.5	104.5	4.6492
4	-12	97	4.5747
5	1	84	4.4308
6	8.5	76.5	4.3373
7	22.5	62.5	4.1352
8.5	35.5	49.5	3.9020
10	44.5	40.5	3.7013
19.5	68.5	16.5	2.8034



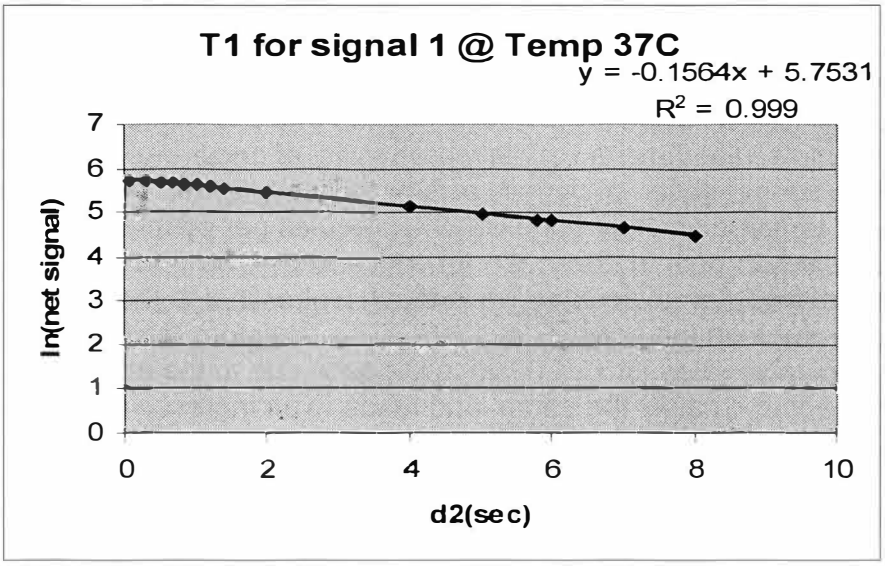
2. Pyruvic acid – No polymer network present – Temperature @ 32 C

d2 (sec)	peak height	Δ signal	ln(Δ signal)
0.1	-82	164.5	5.1029
0.17	-80	162.5	5.0907
0.35	-75	157.5	5.0594
0.6	-72.5	155	5.0434
0.75	-71	153.5	5.0337
0.9	-68	150.5	5.0140
1	-60.5	143	4.9628
2	-48.5	131	4.8752
3	-28.5	111	4.7095
4.5	-6	88.5	4.4830
6	12	70.5	4.2556
7.5	27	55.5	4.0164
9	40	42.5	3.7495
10.5	49	33.5	3.5115
24.5	82.5	0	



3. Pyruvic acid – No polymer network present – Temperature @ 37 C

d2 (sec)	peak height	Δ signal	ln(Δ signal)
0.05	-151	302	5.7104
0.3	-146.5	297.5	5.6954
0.5	-139	290	5.6699
0.65	-133.5	284.5	5.6507
0.8	-128.5	279.5	5.6330
1	-121	272	5.6058
1.2	-113.5	264.5	5.5778
1.4	-105	256	5.5452
2	-81.5	232.5	5.4489
4	-20	171	5.1417
5	5	146	4.9836
5.8	24	127	4.8442
6	27	124	4.8203
7	47	104	4.6444
8	62	89	4.4886



4. Pyruvic acid – Polymer network present – Temperature @ 37 C

d2 (sec)	peak signal
0.550	negative signal
0.600	slightly negative signal
0.610	negligible signal
0.620	slightly positive signal
0.650	positive signal

Results/Discussion:

From the data obtained in the NMR analysis, It was determined that the quantity [$(1/T_1)$] determined for the pyruvic acid sample increased as the temperature increased. This is to be expected since it is known that the diffusion rate of processes occur more rapidly at higher temperatures, and since the quantity [(1/T1)] is proportional to the diffusion rate for both the liquid and gel phases, one would assume that as temperature increased the quantity [$(1/T_1)$] would increase or, in other words, the relaxation time [T_1] would decrease.

From the data, it was also shown that the relaxation time increased nearly ten fold in the polymer gel than in the isolated case. This decrease in the motion of the solvent molecules is due to intermolecular interactions between the polymer network and the solvent molecules.

The theoretical equation that represents the measurements of the relaxation time using NMR is as follows:

$$(1/T_1)^{expt} = (1/T_1)^{intra} + (1/T_1)^{inter}$$

For the isolated case, the term from the intermolecular forces is negligible and therefore the $(1/T_1)$ determined experimentally is mainly due to the intramolecular forces. The intermolecular forces due to the interaction of two pyruvic acid molecules have a very low probability of occurring due to the relatively low concentration of pyruvic acid in the sample. 10.74 mM pyruvic acid is equivalent to approximately 5000 water molecules per pyruvic acid molecule. For the sample with both the polymer network and pyruvic acid however, the contribution of the intermolecular term is much higher due to the amount of interacting protons on the polymer network. This therefore leads to an increase in the experimental value for $(1/T_1)$, since the term due to the intramolecular forces stays approximately the same, and leads to an increase in the relaxation time, which was shown experimentally.

Conclusion:

The motion of the pyruvic acid within the polymer network is about one order of magnitude slower than that in isolated pyruvic acid. This indicates that reactions involving pyruvic acid and possibly other chemical found in biological processes would be better studied in polymer gel matrices which incorporate the same molecular motion that would occur in a biological environment.