The Influence of the Cationic Center, Anion, and Chain Length of Tetra-*n*-alkylammonium and -phosphonium Salt Gelators on the Properties of Their Thermally Reversible Organogels

David J. Abdallah and Richard G. Weiss*

Department of Chemistry, Georgetown University, Washington, D.C. 20057-1227

Received July 13, 1999. Revised Manuscript Received November 22, 1999

The phase properties of 14 tetra-*n*-alkylammonium and -phosphonium salts with chloride, bromide, iodide, and perchlorate as anions and alkyl chain lengths from heptyl to octadecyl have been examined as neat solids and as gelators in thermally reversible organogels. These gelator structures are among the simplest investigated to date. The salts with the longest alkyl chains and a nitrogen cationic center produce the most stable gels based upon temperatures at which gels form on cooling from sols, periods of stability at room temperature, and minimum concentrations of gelator necessary to effect gelation of a liquid at room temperature. Specific gel properties are dependent upon the rate at which their (precursor) sol phases are cooled. Generally, gels with ammonium salts persist for longer periods, require less gelator, and exhibit higher gelation temperatures than those with the corresponding phosphonium salts. Typically, <2 wt % of a gelator is necessary to effect gelation. Several of the gels have persisted without visible change for years when kept at room temperature in sealed containers. The superiority of the tetra-*n*-octadecylammonium salts is attributed to greater dispersive (van der Waals) interactions among alkyl chains and stronger ionic interactions between charged centers. However, since the phosphonium salts are more resistant to thermal decomposition, their liquid mixtures can be cycled between the gel and sol states more times than those with ammonium salts.

Introduction

An organogel is a bicontinuous colloidal system consisting of a small amount (typically $\lesssim$2 wt %) of a microheterogeneously mixed solid network of gelator molecules and a liquid component.[1] The simplest molecules capable of gelling organic liquids are long *n*-alkanes.[2] Stronger intermolecular interactions, induced by insertion of even one heteroatom along an alkane chain,[3] can increase the strength of the gelator strands and, thereby, the stability of their gels.

Here, we examine the properties of a series of charged gelators with two or more heteroatoms, tetra-*n*-alkylylammonium and -phosphonium salts, $H(CH_2)_n)_4Y^+X^-$ (***n*****YX**, where ***n***, the number of carbon atoms per alkyl chain, is varied from 7 to 18, **Y** is N or P, and **X** is Cl, Br, I, or ClO_4), and their thermally reversible organogels[4] with a variety of organic liquids. By systematically changing both the lipophilic and ionic moieties of the ***n*****YX**, we have examined their structural features that promote gelation. Specifically, the effects of changing the chain length ***n***, the size and nature of the cationic center **Y**, and the size of the anion **X** of these salts on their ability to gel various organic fluids have been examined. The nature of the ***n*****YX** should make their gels amenable to several applications involving spectroscopic studies, the formation of microchannels in polymers,[5] and possibly directed electron conduction.

Experimental Section

Instrumentation. Melting points were measured and optical micrographs were recorded on a Leitz 585 SM-LUX-POL microscope equipped with crossed polars, a Leitz 350 heating stage, and an Omega HH21 Microprocessor thermometer connected to a J−K−T thermocouple. Gels for optical microscopy were sealed in 0.8 mm (inside window separation) flattened capillaries to avoid liquid evaporation during heating. Thermally induced phase changes of neat and gelled materials were followed using a TA 2910 differential scanning calorimeter (DSC) interfaced to a TA Thermal Analyst 3100 controller. Samples (3−5 mg of neat materials and 10−20 mg of gels) in open aluminum pans were heated (5 °C/min) under a slow stream of nitrogen; the cooling rate was uncontrolled and depended on the difference between ambient and sample cell temperatures. Cations were characterized by ^1H and ^{31}P NMR (when appropriate) spectroscopies using a Varian 300 MHz spectrometer interfaced to a Sparc UNIX computer with Mercury software. Chemical shifts were referenced to internal TMS (^1H and ^{13}C) or external 85% H_3PO_4 (^{31}P).

Materials. 1-Tetradecylamine (96%, Aldrich), 1-bromotetradecane (97%, Aldrich), tetra-heptylammonium bromide

---

* To whom correspondence should be addressed. Phone: 202-687-6013. Fax: 202-687-6209. E-mail: weissr@gusun.georgetown.edu.

(1) Terech, P.; Weiss, R. G. *Chem. Rev.* **1997**, *97*, 3133.

(2) (a) Srivastava, S. P.; Saxena, A. K.; Tandon, R. S.; Shekher, V. *Fuel* **1997**, *76*, 625. (b) Abdallah, D. J.; Weiss, R. G. *Langmuir*, in press.

(3) Abdallah, D. J.; Lu, L.; Weiss, R. G. *Mater. Chem.* **1999**, *11*, 2907.

(4) (a) Lu, L.; Weiss, R. G. *Chem. Commun.* **1996**, 2030. (b) Lu, L.; Weiss, R. G. *Langmuir* **1995**, *11*, 3630.

(5) Gu, W.; Lu, L.; Chapman, G. B.; Weiss, R. G. *Chem. Commun.* **1997**, 543.

10.1021/cm990437+ CCC: $19.00

(**7NBr**; 98%, Aldrich; mp 90.1−91.4 °C; lit.[6] mp 88.9−89.1 °C), tetra-decylammonium bromide (**10NBr**; 95%, TCI; mp 88.4−90.9 °C; lit.[7] mp 90.4 °C), tetra-dodecylammonium chloride (**12NCl**; 97%, Fluka; mp 80.7−82.7 °C), tetra-dodecylammonium iodide (**12NI**; 98%, Lancaster; mp 114.5−116.6 °C; lit.[8] mp 116 °C), tetra-dodecylammonium bromide (**12NBr**; Fluka; 99%; mp 88.1−91.8 °C; lit.[7] mp 89.6 °C), tetra-hexadecylammonium bromide (**16NBr**; 98%, Aldrich; mp 100.4−101.1 °C; lit.[7] mp 104.7 °C), tetra-octadecylammonium bromide (**18NBr**; 98%, Aldrich; mp 103.7−104.8 °C; lit.[7] mp 106.9 °C), and tetra-octadecylammonium perchlorate (**18NClO$_4$**; 98%, Fluka; mp 108.4−113.4 °C) were used as received. Tetra-octadecylammonium iodide[9] (**18NI**; mp 113.3−114.4 °C), tetra-decylphosphonium bromide[10] (**10PBr**; mp 53.6−57.0 °C), tetra-octadecylphosphonium bromide[11] (**18PBr**; mp 92.3−94.8 °C), and tetra-octadecylphosphonium iodide[10] (**18PI**; mp 97.6−99.3 °C) were available from previous work.

Tetra-tetradecylammonium Bromide (14NBr). **14NBr** was synthesized by a modification of the procedure of Eriksen et al.[8] A solution of 453 mg (2.12 mmol) of 1-tetradecylamine, 25 mL of absolute ethanol, and 2.53 mL (8.50 mmol) of 1-bromotetradecane was refluxed for 3 days with periodic addition of 5% ethanolic potassium hydroxide to maintain pH ∼9 (wet universal indicating paper). During the reflux period, a white, water-soluble precipitate, presumably NaBr, appeared. The mixture was filtered hot, and the filtrate became a gel-like suspension as it cooled. The gel was mechanically destroyed and refiltered. The solid, a combination of tri-tetradecylamine and tetra-tetradecylammonium bromide, was washed with warm (∼40 °C) hexane. Recrystallization from 1-propanol afforded 101 mg (5.4%[12]) of a white solid: mp 93.1−94.0 °C; ^{1}H NMR (CDCl$_3$) δ 3.28 (s, 8H), 1.57 (s, 8H), 1.15 (broad s, 88H), 0.78 (t, $J = 6.3$ Hz, 12H) ppm; ^{13}C NMR (CDCl$_3$) δ 59.1, 31.8, 29.6 (broad), 26.8, 26.4, 22.6, 22.3 ppm.

Tetra-octadecylphosphonium Perchlorate (18PClO$_4$). To a solution of 6.0 g (5.3 mmol) of **18PBr** in 200 mL of CHCl$_3$ was added 6.0 g (38 mmol) of potassium ethyl xanthate.[13] After being stirred for 24 h, the yellow solution was filtered. The intermediate, tetra-octadecylphosphonium ethyl xanthate, was isolated by evaporating the filtrate to residue and recrystallizing it from *tert*-butyl methyl ether to afford 3.6 g (57%) of a yellow solid: mp 51.4−54.3 °C; ^{1}H NMR (CDCl$_3$) δ 4.49 (q, $J = 7.2$ Hz, 2H), 2.42 (m, 8H), 1.50 (m, 16H), 1.37 (t, $J = 7.2$ Hz, 3H), 1.25 (m, 112H), 0.88 (t, $J = 6.3$ Hz, 12H) ppm. Concentrated perchloric acid (5.0 mL; 35 mmol) was added to 25 mL of a chloroform solution containing 500 mg (0.43 mmol) of tetra-octadecylphosphonium ethyl xanthate. After being stirred for 1 h, the solution was extracted with HPLC grade water (5 × 20 mL), and the organic layer was reduced to a solid residue on a rotary evaporator. Recrystallization from *tert*-butyl methyl ether and a small amount of chloroform afforded 398 mg (81%) of a white solid: mp 93.2−94.6 °C; ^{1}H NMR (CDCl$_3$) δ 2.20 (m, 8H), 1.50 (m, 16H), 1.25 (m, 112H), 0.88 (t, $J = 6.6$ Hz, 12H) ppm; ^{31}P NMR (CDCl$_3$) δ 33.29 ppm.

Gelation Studies. Samples for gelation studies were prepared by placing known amounts of solvent and an ***n*YX** salt in a 5 mm (i.d.) glass tube sealed at one end. The other end was flame-sealed and the samples were twice heated until the solid dissolved and cooled to room temperature before making measurements. Gelation was considered successful if no sample flow was observed upon inverting the container (i.e., the inverse flow method[14]) after a third heating and cooling cycle. If part of the sample fell, the sample was classified as a partial gel. Samples that fell entirely were characterized as either a solution or a precipitate (and liquid), depending on their physical appearance. Three different cooling protocols were used to form gels from hot solutions: sealed tubes were submerged in 500 mL of stirred and initially boiling water and were kept there until the water returned to room temperature (slow cooling); tubes were removed from the boiling water and cooled in the air (moderate cooling); tubes were removed from the boiling water and placed under a stream of water at 20 °C (fast cooling).

The gel transition temperature (T_{gel}) was measured when a solidlike gel, inverted in a thermostated water bath, became fluidlike (i.e., fell under the influence of gravity). Ranges of T_{gel} were recorded from the start of sample flow until the entire sample had fallen. Some T_{gel} measurements were made by DSC, also. T_{gel} values from thermograms are averages of the onset of transitions observed on heating and cooling.

Samples for DSC analyses were transferred to aluminum pans in their gelled state (for experiments to probe the influence of different cooling protocols) or as hot solutions (for all other measurements).

Results and Discussion

Some solid phases of ***n*NX** salts (**X** = halogen) are conformationally disordered (i.e., condis) crystals.[7] Recently, we explored the influence of ***n***, **Y**, and **X** on the conformations and packing of several ***n*YX** in their crytalline phases.[10] Upon being heated, many of the salts display more than one solid−solid phase transition between room temperature and their clearing points. Regardless of whether the packing of ***n*YX** molecules in gel strands is the same as in their neat crystalline or condis phases,[15] it is clear that subtle modifications of ***n*** or **X**, especially, can cause drastic changes in solid state conformations.

Preliminary studies have demonstrated that simple quaternary ammonium salts also form organogels.[4] One of these gelators (**18NBr**) has been used to construct “reverse aerogels”[5] whose strand cross sections are ∼0.5−10 μm. A key to producing such materials is the ability of a salt to gel easily polymerizable monomers. The data presented indicate that several of the ammonium and phosphonium salts investigated here can do so.

In addition, ***n*YX** salts lack the structural complexity inherent to many other gelators.[1] Their simplicity allows the relationships between gelator structure and gelation ability to be investigated more directly. Only three structural permutations are possible in ***n*YX** salts: chain length, nature and size of the anion, and nature and size of the cationic center. The influence of each of these structural factors, as well as the influence of the rate of cooling rates of sols, on gelation efficiency has been investigated.

Thermodynamic Properties of Neat Gelators. Temperatures and enthalpies of transition of the salts are summarized in Table 1. Data for all of the ***n*NBr** salts, except ***n*** = 14, have been reported previously.[7]

---

(6) Gordon, J. E. *J. Am. Chem. Soc.* **1965**, *87*, 4347.

(7) Xenopoulos, A.; Cheng, J.; Yasuniwa, M.; Wunderlich, B *Mol. Cryst. Liq. Cryst.* **1992**, *214*, 63.

(8) Eriksen, S. P.; Tuck, L. D.; Oneto, J. F. *J. Org. Chem.* **1960**, *25*, 849.

(9) Lu, L.; Sharma, N.; Nagana Gowda, G. A.; Khetrapal, C. L.; Weiss, R. G. *Liq. Cryst.* **1997**, *22*, 23.

(10) Abdallah, D. J.; Perlstein, J.; Bachman, R. E.; Weiss, R. G. *J. Phys. Chem. B* **1999**, *103*, 9269.

(11) Abdallah, D. J.; Robertson, A.; Hsu, H.-F.; Weiss, R. G. *J. Am. Chem. Soc.*, submitted for publication.

(12) The yield of **14NBr** was much lower than that reported for **14NI** since elimination reactions occur more readily with alkyl bromides.

(13) (a) Rao, S. R. *Xanthates and Related Compounds*; Dekker: New York, 1971. (b) A method based on that described: Supulveda, L.; Cabrera, W.; Gamboa, C.; Meyer, M. *J. Colloid Interface Sci.* **1987**, *117*, 460.

(14) Takahashi, A.; Sakai, M.; Kato, T. *Polym. J.* **1980**, *12*, 335.

(15) Ostuni, E.; Kamaras, P.; Weiss, R. G. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1324.

Table 1. Transition Temperatures and Enthalpies (ΔH) from DSC Thermograms of nYX Salts. Last Row for Each Salt Entry Corresponds to the Onset of a Solid-isotropic Transition; All Others Are for Solid−Solid Transitions

	first cycle				second cycle	
	heating		cooling		heating	
	T (°C)[a]	ΔH (kJ/mol)[b]	T (°C)[a]	ΔH (kJ/mol)[b]	T (°C)[a]	ΔH (kJ/mol)[b]
7NBr	63.2	4.1	56.6	5.1	62.9	4.5
	86.9	34.5	79.0	32.0	86.4	33.3
10NBr	54.2	1.4	[c]	[c]	44.4	1.2
	71.3	56.0	67.5	50.4[d]	71.2	53.3
	79.7	29.1	78.5	28.3[d]	78.0	27.4
10PBr	51.0	76.1	42.6	76.4[d]	50.5	70.5
12NCl	[c]	[c]	64.8	99.7[e]	[c]	[c]
	71.9	105.0[d]	67.0	10.1[e]	69.3	110.0[d]
12NBr	[c]	[c]	[c]	[c]	40.3	4.0
	[c]	[c]	55.9	13.6	60.2	8.5
	70.3	32.0	80.7	5.7	68.0	5.5
	86.7	66.7	83.8	62.8	85.8	69.0
12NI	63.6	1.9	63.7	13.6[e]	65.3	2.4
	73.7	26.4	69.5	20.4[e]	73.8	29.1
	84.1	2.6	87.9	1.9	86.1	3.3
	111.1	42.6	109.3	41.3	111.3	42.3
14NBr	82.1	41.0[e]	73.7	22.2	82.9	29.1
	91.6	89.1[e]	86.6	85.7[d]	87.2	92.1[d]
16NBr	92.4	76.2	87.9	72.8	92.7	84.3
	99.7	100.6	95.7	97.1	99.1	91.9
18NBr	[c]	[c]	42.3	16.4	47.0	17.5
	51.6	16.0	93.3	53.3[e]	[c]	[c]
	98.7	164.4[d]	97.3	90.8[e]	97.2	169.1[d]
18NI[8]	82.1	11.7	80.1	13.4	82.1	12.7
	113.8	115.6	111.0	120.0	113.6	115.7
18PBr	[c]	[c]	[c]	[c]	87.6	49.5[e]
	94.8	201.6	83.6	185.6	94.6	129.1[e]
18PI	[c]	[c]	[c]	[c]	92.4	5.6[e]
	97.8	143.2[d]	92.9	154.8	97.2	145.6[e]
18NClO$_4$	67.4	0.4	77.9	3.8	75.3	5.1
	76.5	1.7	81.9	0.6	83.6	0.8
	105.2	84.8[e]	107.7	59.4	105.1	60.5[e]
	106.0	8.2[e]	108.7	42.1	110.0	37.2[e]
18PClO$_4$	57.1	1.3	[c]	[c]	[c]	[c]
	64.5	1.6	[c]	[c]	[c]	[c]
	91.4	119.6	88.7	129.7	91.4	124.4

[a] Peak onset. [b] Per mole of gelator. [c] No transition observed. [d] Includes shoulder peak. [e] Two overlapping peaks.

Table 2. Melting Temperatures (°C) of Related Quaternary Ammonium and Phosphonium Salts, $(H(CH_2)_n)_aY(CH_3)^+{}_{4-a}X^-$

			Y	
a	n	X	N	P
1	12	I	237[a]	87−88[b]
2	10	Cl	59 (T_{KS}), 94 (T_{SI})[14]	38 (T_{KS}), 155 (T_{SI})[14]
	14	Cl	48 (T_{KS}), 70 (T_{SI})[14]	68 (T_{KS}), 187 (T_{SI})[14]
	18	Cl	85 (T_{KS}), 122 (T_{SI})[14]	82 (T_{KS}), 145 (T_{SI})[14]
3	18	I	103.1 (T_{KS}), 121.9 (T_{SI})[8]	72.1 (T_{KS}), 112.7 (T_{SI})[10]
4	5	Br	98.7−99.85	49.5−51[c]
	5	I	139[d]	96−98[e]
	6	Br	104[d]	45−46[c]
	6	I	102−103[7]	48−50[e]
	7	I	123[d]	80−82[e]
	8	Br	95[f]	45−47[e]
	8	I	127[7]	87−88[e]
	10	I	118−120[7]	71−74[e]

[a] Beckett, A. H.; Woodward, R. J. *J. Pharm. Pharmacol.* **1963**, *15*, 422. [b] Hays, H. G. *J. Org. Chem.* **1966**, *31*, 3817. [c] Tsentovskii, V. M.; Barabanov, V. P.; Kharrasava, F. M.; Busygina, T. A. *J. Gen. Chem. USSR* **1971**, *41*, 1667. [d] Coker, T. G.; Ambrose, J.; Janz, G. J. *J. Am. Chem. Soc.* **1970**, *92*, 5293. [e] Feshchenko, N. G.; Mazepa, I. K.; Makovetskii, Y. P.; Kirsanov, A. V. *J. Gen. Chem. USSR* **1969**, *39*, 1846. [f] Danilova, O. I.; Esikova, I. A.; Yufit, S. S. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1986**, *35*, 2215.

Our numbers have been used to ensure that the total data set was collected under the same experimental conditions. The literature values and ours differ slightly for **10NBr** and **18NBr**; we observed an additional small transition for **10NBr** at 54.2 °C, and a lower clearing temperature and an additional small transition for **18NBr** during the first cooling at 42.3 °C and the second heating at 47.0 °C.

As do salts with two[16] or three[11] long alkyl chains, phosphonium salts with *four* long alkyl chains exhibit simpler DSC thermograms and lower melting temperatures than the corresponding ***n*NX** (Tables 1 and 2). Using thermogravimetric analyses, Kanazawa et al.[16] found that ammonium salts decompose at lower temperatures than phosphonium salts of analogous structure. Also, ***n*PX** are more stable thermally than ***n*NX**. After being heated for 18 h at 110 °C, **18NBr** had a broadened melting transition that was depressed by ~9° and required only $^2/_3$ of the heat input of a pristine sample. Only subtle changes were apparent in the thermograms of heated **18PBr**. Peaks were broadened slightly, but occurred at the same temperatures and with the same heat contents as before heating. We suspect that Hofmann-type eliminations with the ***n*NBr** salts become important at elevated temperatures. Since thermoreversibility is also an important characteristic of organogels, the phosphonium salts may be more suitable in applications where continuous re-forming of a gel is desired.

The melting temperatures of ***n*PBr** salts increase as the chain length ***n*** is increased from 10 to 18. Melting temperatures of ***n*NBr** salts *decrease* as ***n*** increases to 7 and then *increase* thereafter.[7] Presumably, chain packing interferes with the more important ionic interactions in the salts with short chains, but dispersion forces between chains dominate the overall packing energy at ***n*** > 7, leading to a change in morphology.[10] By contrast, melting temperatures of ***n*NI** salts *decrease*[8] as ***n*** increases beyond 8.

Qualitative Gelation Tests. Mixtures of ***n*YX** salts and various alkanes, alkenes, alkanols, or aromatic liquids were tested for gelation using the three cooling protocols described in the Experimental Section. Data in Table 3 assess via transition temperatures (T_{gel}) and persistence times the influence of gelator concentration and alkyl chain length on the stability of ***n*NBr** gels in various organic fluids. Comparisons of stabilities of gels composed of salts with different **Y** and **X** groups are presented in Table 4.

Gel formation and T_{gel} values were reproducible usually from run-to-run or from sample-to-sample. However, somewhat sporadic behavior was observed in samples near the critical gelator concentration (CGC; i.e., the lowest concentration of gelator at which gels could be formed at room temperature according to the inverse flow technique). At these concentrations, stochastic behavior may be brought on by seemingly innocuous differences in the way a sample was prepared or cooled; "identical conditions" has a different practical meaning near the CGC and at much higher gelator concentrations. Also, gels with longer chained gelators behaved more reproducibly near the CGC. Traces of

---

(16) Kanazawa, A.; Tsutsumi, O.; Ikeda, T.; Nagase, Y. *J. Am. Chem. Soc.* **1997**, *119*, 7670.

Table 3. Transition Temperatures, T_{gel} (°C), and Periods of Stability (at room temperature)[a] of Gels with *n*NBr Gelators

		concentration		cooling rate (T_g, °C)		
liquid	gelator	wt %	mM	slow	moderate	fast
hexadecane	**7NBr**		200		p	
	10NBr	14.57	200		58 (<2 d)	
	12NBr	0.99	10	76	pg 45−65 (1h)	55−74
		1.96	20	78	79 (<2 d)	54−77
		3.83	40	78	77 (<2 d)	59−65
	14NBr	1.13	10	74	73 (2 w)	65−67
		2.23	20	74	73 (>2 y)	74
		4.37	40	74	79 (>2 y)	76
	16NBr	1.28	10	76−77	80 (>2 y)	73
		2.51	20	87	74 (>2 y)	67
		2.61	40	85−86	81 (>2 y)	74
	18NBr	1.41	10	84−86	79−85 (>2 y)	73
		2.79	20	86−89	85 (>2 y)	77−86
		5.47	40	89−90	87 (>2 y)	85−87
dodecane	**7NBr**		≤200		p	
	12NBr	1.02	10		p	
		2.02	20	p	p	g
		4.89	50	74	g (<2 d)	g
	14NBr	1.16	10		p	
		2.43	20	p	p	pg
		5.56	50	pg	g (<2 d)	g
	16NBr	1.31	10	75−79	p	p
		2.59	20	75−81	74 (>2 y)	75
		6.22	50	82−85	79 (>2 y)	82
	18NBr	1.50	10		p	
		2.87	20	g	74 (>1 m)	78
		6.88	50	g	79 (>1 m)	80
benzene	**7NBr**		≤200		s	
	10NBr	13.1	200		s	
	12NBr	0.87	10	s	s	24−29
		1.73	20	p	p	30
		3.00	35	p	p	30
		4.23	50	29	29 (<2 d)	30
	14NBr	1.00	10	39−43	40 (1 d)	38−41
		1.98	20	39−40	40 (<2 d)	38
		3.42	35	39−40	43 (2 y)	38
		4.81	50	39−41	43 (2 y)	39
	16NBr	1.13	10	45	43 (<2 d)	47
		2.23	20	49	51−53 (2 w)	47
		3.83	35	50−53	52−53 (>2 y)	50−51
		5.39	50	51	54 (>2 y)	51−52
	18NBr	1.25	10	60	56 (>3 w)	55−56
		2.47	20	59	58 (>2 y)	56
		4.25	35	60	58 (>2 y)	57−60
		5.96	50	60	56 (>2 y)	53
1-octanol	**7NBr**		≤200		s	
	10NBr	13.8	200		s	
	12NBr	6.13	70		s	
	14NBr	6.96	70		s	
	16NBr	2.28	20		p	
		5.68	50	37−41	pg (>2 y)	pg 41
		7.77	70	38−44	g (>2 y)	42
	18NBr	2.60	20	49	p	49
		6.28	50	50−55	g (>2 y)	53
		8.57	70	54−55	g (>2 y)	54
CCl_4	**7NBr**		≤200		s	
	10NBr	7.6	200		s	
	12NBr	4.60	100		s	
	14NBr	5.25	100		s	
	16NBr	1.24	20		p	
		5.88	100	45	41 (3 d)	45
	18NBr	1.38	20		s	
		6.50	100	g	48 (>1 w)	g
MMA[b]	**7NBr**		≤200		s	
	10NBr	12.34	200		pg 35	
	12NBr	0.82	10	p	p	pg 21−35
		1.62	20	p	36−37	pg 34−35
		3.96	50	47	43	39
		6.18	80	48	44	42
	14NBr	0.94	10	p	45−46	pg 39−48
		1.85	20	50	47−49	39−50
		4.51	50	49−50	50	44
		7.02	80	49	51	48
	16NBr	1.05	10	58	51−58	pg 42−48
		2.08	20	60	60−62	48
		5.05	50	68	65−66	64−69
		7.84	80	70	66	68−69
	18NBr	1.17	10	67	65	26−48
		2.31	20	70−73	69	69−74
		5.59	50	76	71	71−74
		8.65	80	76	74	73−76
styrene	**7NBr**		≤200		s	
	10NBr	12.66	200		s	
	12NBr	0.84	10	p	p	p
		1.67	20	p	p	26−29
		4.07	50	p	p	30
		6.36	80	30	31	30
	14NBr	0.96	10	p	p	31−33
		1.91	20	p	36−37	34−35
		4.63	50	40	39	37
		7.21	80	41	40	40
	16NBr	1.08	10	48−51	48	44−46
		2.14	20	54	49−52	49−52
		5.19	50	55	54−55	55
		8.06	80	56	54−56	55−57
	18NBr	1.20	10	p	pg 59	56
		2.38	20	60−61	59−60	57
		5.74	50	60−61	56−60	57−59
		8.88	80	63	62	61
GMA[c]	**7NBr**		≤200		s	
	10NBr	11.23	200		44	
	12NBr	0.73	10	p	p	34
		1.46	20	p	43	39
		3.57	50	p	41−45	40
		5.59	80	p	44	44
	14NBr	0.84	10	p	50	44
		1.67	20	62	58	46
		4.07	50	64	62	53
		6.35	80	64	62	61
	16NBr	0.95	10	74−75	68	54
		1.88	20	74	71	54
		4.56	50	75	77−79	75
		7.10	80	78	77−79	81
	18NBr	1.05	10	76	77	59
		2.08	20	76	84	71−75
		5.05	50	83	84	84
		7.84	80	84	86	84

[a] Periods of stability in parentheses: h = hour; d = day; w = week; m = month; y = year. Abbreviations: g, gel formed but T_{gel} not determined; pg, partial gel; where gels did not form, s = solution, p = solid + liquid. [b] MMA = methyl methacrylate. [c] GMA = glycidyl methacrylate.

ionic impurities are expected to have a larger influence on gelator strands comprised of ***n*YX** with shorter chains. Especially when gelator concentrations were near the CGC, the ability of an inverted gel to resist flow was dependent upon the diameter of its sample tube. In wider tubes than the standard 5 mm (i.d.), higher CGCs were required because the force of gravity on the liquid is exerted proportionately more on the gelator strand networks than on the vessel walls.

Most gels of the ammonium and phosphonium salts were milky white in appearance. Nearly transparent gels were obtained near the CGC with aromatic liquids

Table 4. Transition Temperatures, T_{gel} (°C), and Periods of Stability (at room temperature)[a] of Gels with *n*YX Gelators

gelator	conc (M)	liquid hexadecane	 benzene	 1-octanol
12NCl	0.02	53 (4 d)		
	0.08	62−64 (>1 m)	s	s
12NBr	0.02	74 (3 d)		
	0.08	59 (1 d)	s	s
12NI	0.02	86−88 (>1 m)		
	0.08	88−90 (>1 m)	s	s
10NBr	0.2	58 (<2 d)	s	s
10PBr	0.2	40 (1 h)	s	s
18NBr	0.01	85 (>1 m)	55[b] (>1 m)	49[b] (0.02 M, >1 m)
18PBr	0.01	70 (>1 m)	47[b] (3 w)	46[b] (0.02 M, >1 m)
18NI	0.01	65−86 (>2 y)	p	p
18PI	0.01	75 (>2 y)	44[b] (1 w)	p
18NClO$_4$	0.01	81 (>1 m)	41 (>1 m)	59 (>2 y)
18PClO$_4$	0.01	73 (1 w)	32 (1 w)	56 (>1 m)

[a] Periods of stability in parentheses: h = hour; d = day; w = week; m = month; y = year. T_{gel} was determined after moderate cooling. [b] T_{gel} was determined after fast cooling. Where gels did not form: s = solution, p = solid + liquid.

such as styrene and benzene when the fast-cooling protocol and long-chained gelators were employed. Higher gelator concentrations increased opacity.

Dependence of Chain Length on Gelation By *n*YX Salts. Due to its high solubility in all of the liquids tested, **7NBr** was unable to form a gel. Relatively high concentrations (~0.2 M) of the slightly longer **10NBr** gelled hexadecane (stable up to 2 days) and glycidyl methacrylate, but not benzene, 1-octanol, carbon tetrachloride, or styrene. Generally, as ***n*** of the ***n*NBr** increased, the CGC decreased and T_{gel} values increased. The trends in melting temperatures of the gelators and T_{gel} of their gels parallel each other. Gels formed from salts with shorter chains usually had wider T_{gel} ranges and were stable for shorter periods. This indicates that the change in solubility of these gelators with temperature is more gradual than when the chains are longer. Consequently, a clear assignment of T_{gel} using the inverse flow method was not always possible for gels of ***n*NBr** with shorter chains.

In addition to increasing in T_{gel} and lowering CGCs, longer gelator chain lengths extend periods of stability (Table 3). For instance, within the range of **16NBr** and **18NBr** gelator concentrations examined and at the higher concentrations of **14NBr**, hexadecane gels have been stable for more than 2 years! By contrast, hexadecane/**12NBr** gels were stable for no more than 2 days. The other liquids examined in Table 3 follow qualitatively the same trend. CCl_4/**16NBr** and CCl_4/**18NBr** gels, which required > 5 wt % gelator, persisted for less than 1 week and became yellow with time (indicating that some decomposition had occurred).

Figure 1 is a compilation of heating thermograms for gelled samples consisting of 0.01 and 0.08 M ***n*NBr** in hexadecane. The rate of heating was constant for all of the samples within one series. A weak, broad, lower temperature transition can be detected in some thermograms from 0.08 M gels. The trend toward higher T_{gel} as ***n*** increases is ascribed to increasing *weight %* of gelator and greater dispersion forces between chains as they become longer. The heats (per gram of sample) also increase with chain length to ***n*** = 16, but not between **16NBr** and **18NBr**. Since samples were in open pans and some evaporation of the liquid occurred, the trends in the thermograms are only qualitatively correct.

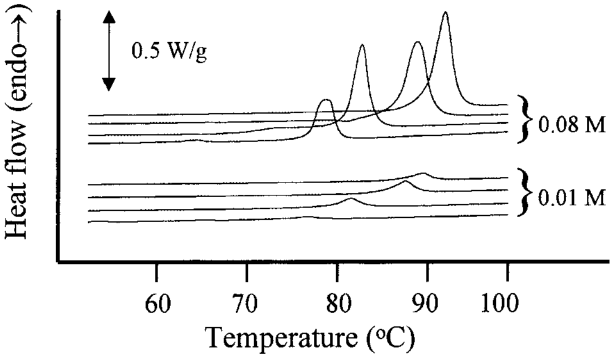

Figure 1. DSC heating thermograms of fast-cooled ***n*NBr**/hexadecane gels at 0.01 and 0.08 M gelator concentrations. The values of ***n*** for each concentration are in the order 12 → 14 → 16 → 18 from bottom to top.

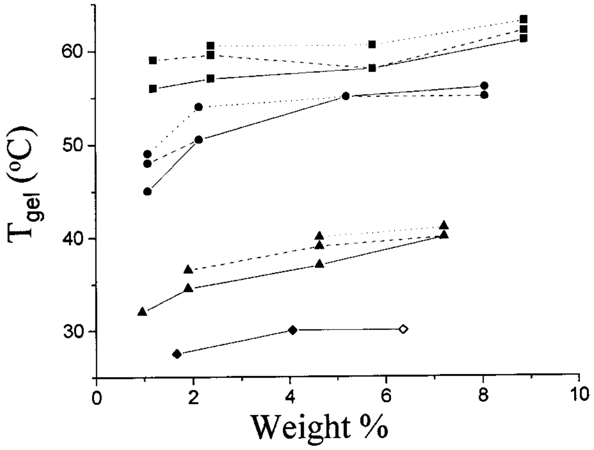

Figure 2. The influence of cooling rates of ***n*NBr**/styrene sols on the T_{gel} values of their gels: ***n*** = 18 (■), 16 (●), 14 (▲), and 12 (◆, ◇); fast (—), moderate (- - -) and slow (···) cooling. Averages are reported when ranges of melting were noted. The ◇ value is the same for fast, moderate, and slow cooling.

Thermograms in Figure 2 also demonstrate the dependence of alkyl chain length of ***n*NBr** gelators on gelation ability. Salts with the longest chains provide gels with the highest T_{gel} values, regardless of cooling protocol, and the lowest CGCs. If the packing of gelator molecules in gel strands is microscopically separated into lipophilic and lipophobic regions (as in their bulk solid states[10]), longer alkyl chain lengths will increase the London dispersion forces that supplement the source of primary stabilization, electrostatic interactions.[10]

Of special note is the observation that a wide range of ammonium bromide salts were able to gel methyl methacrylate, styrene, and glycidyl methacrylate (Table 3). As before, gelators with longer chains provided the more stable gels. Each of these should be convertible to “reverse aerogels” after polymerization and removal of the gelator strands.[5] In addition, we find that the ***n*PBr** also gel these monomers. Since the phosphonium gelators are thermally more stable (vide infra) and have lower T_{gel} values in general than the corresponding ***n*NBr** salts, there are reasons to believe that the phosphonium gels may produce more homogeneous channels in the aerogels.

Dependence of the Anion and Cation on Gelation by *n*YX Salts. For gels with the same liquid and concentration of **10YBr 18YBr**, and **$18YClO_4$**, T_{gel} values are higher when **Y** = N than **Y** = P. *If* the same packing motifs are present in gelator strands and bulk crystals,[15] the higher gelation temperatures of the ammonium salts are easily explained by the melting temperatures of the neat salts. Apparently, the markedly lower solubility of **18NI** than **18PI** in the liquids tested is more important than melting temperatures in controlling T_{gel}. If, as we suspect, the lower solubility also results in some bulk crystallization of the ammonium salt in competition with strand formation, the *effective* concentration of **18NI** in gelator strands is less than the bulk concentration (and T_{gel} is lowered as a consequence).

In addition to their higher T_{gel} values, gels of ammonium salts exhibit lower CGCs and persist for longer periods than those of the corresponding phosphonium salts. For example, the CGC values of benzene gels are 0.004 M (0.53 wt %) for **$18NClO_4$** and 0.01 M (1.3 wt %) for **$18PClO_4$**. The dependence of gel lifetimes on **Y** is apparent for **$18YClO_4$** gels with hexadecane, benzene and 1-octanol as liquids (Table 4).

Any alterations within the ionic region of a gelator assembly that either enhance or destabilize electrostatic interactions will affect the stability of the strands. For example, electrostatic attractions between a quaternary cationic center and its associated anion are smaller when **Y** = P than when **Y** = N. Polarizability of the cationic center does not appear to play a role since the valence shell electrons about **Y** are well shielded from the anion by the four alkyl chains.[10] However, greater ionic interactions can result from tighter packing of the α and β methylene units near N. Since N−C covalent bond distances (~1.53 Å) are shorter than P−C ones (~1.81 Å),[10] N^+ can be closer to its anions than can P^+. Additionally, the larger inductive effects[17] of nitrogen make the α and β methylene hydrogen atoms of ***n*N^+** more acidic (i.e., bear a larger partial positive charge) than those of ***n*P^+**; stronger hydrogen bonding and, therefore, shorter hydrogen−anion contact distances with the anions are expected for the ammonium salts.

These electronic differences between nitrogen and phosphorus help explain several sets of observations, including the following: (1) why melting temperatures of ***n*PX** and melting and solid−liquid−crystalline transition temperatures of phosphonium salts with three long alkyl chains and a fourth shorter one are lower than those of the corresponding ammonium salts (Table 2); (2) why lower concentrations of ammonium salts are needed to effect gelation, and the temporal stability of their gels is greater. An exception to these trends, lower T_{gel} values of **18NI** than **18PI** organogels, may be related to molecular packing arrangements within the strands.[15] Currently, we lack sufficient data to address this point further.

No clear trend between neat melting temperatures or T_{gel} values and anion size of the **$12N^+$**, **$18N^+$**, and **$18P^+$** cations is discernible from the data in Table 4. Comparison of gelling properties of several anions with one cation must take into consideration not only the sizes of the anions, but also their "hardness",[18] distance from and interation with the **Y^+** atom, and their influence on conformations of methylene groups nearby.[10] On a more global level, each of these factors may influence the solubility of a salt in (and, therefore, its ability to gel) a liquid.

Dependence of Gel Formation on Cooling Rate. The largest differences among gels formed according to the three cooling protocols described in the Experimental Section were observed near the CGC. Fast cooling led to gelation in several instances where moderate or slow cooling did not (Table 3). Since dilute fast-cooled gels were more translucent than those cooled more slowly (vide infra), gelator networks of the fast-cooled gels are more intricate and have larger surface/gelator mass ratios. Therefore, they can entrap a larger volume of liquid by surface tension[1] than the slower-cooled gels. For example, fast-cooled samples of **18PBr** or **18PI** in aromatic liquids provided translucent gels with a bluish tint (Tyndall effect), but the same samples formed white and opaque gels when slowly cooled from the sol state.

The dependence of cooling protocol on T_{gel} and gelation is also evident in Figure 2. Values of T_{gel} are higher for slowly cooled, gels; however, the probability of gelation is higher when sols are cooled quickly.

18PBr/styrene gels with low gelator concentrations were examined by optical microscopy (Figure 3). Gelator strands are easily distinguished at higher concentrations or when the gels were prepared by slow cooling. No strands were discernible at the same magnification in fast-cooled styrene gels with low gelator concentrations. Gels formed by moderate cooling rates exhibited thinner strands than those from slow cooling. **18PBr**/hexadecane gels were not translucent regardless of the cooling protocol. The fast-cooled gels were less opaque, and optical micrographs of the slow-cooled gel indicated the presence of platelike microcrystallities rather than strands (Figure 4). Results similar to those in Figure 3 were obtained for **18PI**/benzene gels (Figure 5). Longer and/or thicker strands are present in slow-cooled gels.

Thermograms of **18PBr**/styrene and **18PBr**/hexadecane gels, taken immediately after their formation by the three cooling protocols (Figures 3 and 4), show slight differences in shape and T_{gel}, but the heat of melting and breadth of the transitions increase from the fast- to the slow-cooled samples. Since the same protocols were followed to obtain the data in Figures 3−5 as those in Figure 1, the trends are valid only qualitatively and when compared internally.

The larger strands (of the slow-cooled gels) require longer to melt, making their transition peaks broader. The lower T_{gel} values measured by the inverse flow method and by DSC for fast cooled gels are a consequence of the larger contact area between the liquid and smaller and narrower strands. Assuming that the same fraction of gelator is incorporated into the strands regardless of the cooling protocol (i.e., the solubility of the gelator in the liquid component is independent of the cooling protocol and the gelator strands are at equilibrium with the liquid), the enthalpic differences can be ascribed to varying heats of dissolution that

---

(17) The through-space field inductive parameters for $N(CH_3)_3^+$ and $P(CH_3)_3^+$ are 0.99 and 0.75, respectively.[17a] These values are a good indicator that quaternary ammonium cations have a greater affinity for electrons than quaternary phosphonium cations: (a) Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165.

(18) Pearson, R. G. *Chemical Hardness*; Wiley-VCH: Weinheim, Germany, 1997; Chapter 1.

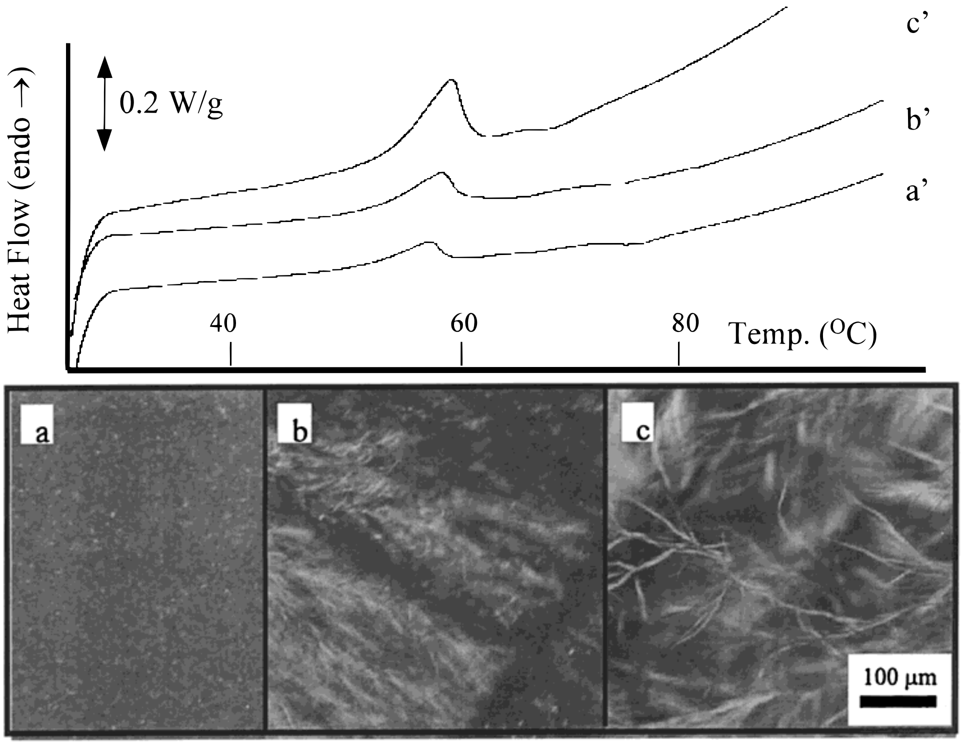

Figure 3. Optical micrographs (a, b, and c) at room temperature and DSC heating thermograms (a′, b′, and c′) of 0.01 M (1.2 wt %) **18PBr**/styrene gels prepared by fast (a and a′), moderate (b and b′), and slow (c and c′) cooling (see text).

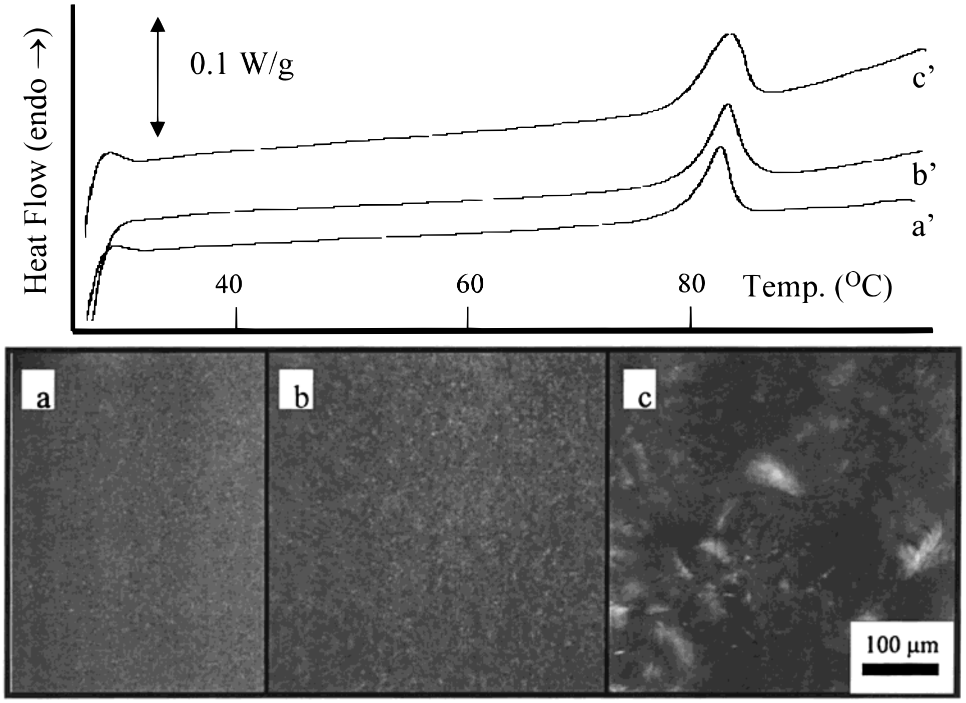

Figure 4. Optical micrographs (a, b, and c) at room temperature and DSC heating thermograms (a′, b′, and c′) of 0.01 M (1.4 wt %) **18PBr**/hexadecane gels prepared by fast (a and a′), moderate (b and b′), and slow (c and c′) cooling (see text).

accompany the melting of gelator strands. A larger fraction of gelator molecules in fast-cooled gels is initially in contact with the liquid component before heating. The single peak in the thermograms is consistent with the presence of only one morph in the strands.

Conclusions

Ammonium salts have higher T_{gel} values, are stable for longer periods, and require lower concentrations to gel organic liquids than phosphonium salts with corresponding structures. Stronger $\mathbf{N}^+\ \mathbf{X}^-$ than $\mathbf{P}^+\ \mathbf{X}^-$ interactions are believed to play a major role in these observations. Also, salts with longer chains gel more efficiently than those with shorter chains. Longer alkyl chains on ***n*****YX** salts strengthen gel strands due to increased gelator–gelator-induced London dispersion forces (which supplement the stronger $\mathbf{Y}^+\ \mathbf{X}^-$ electrostatic interactions). No correlation between the size or

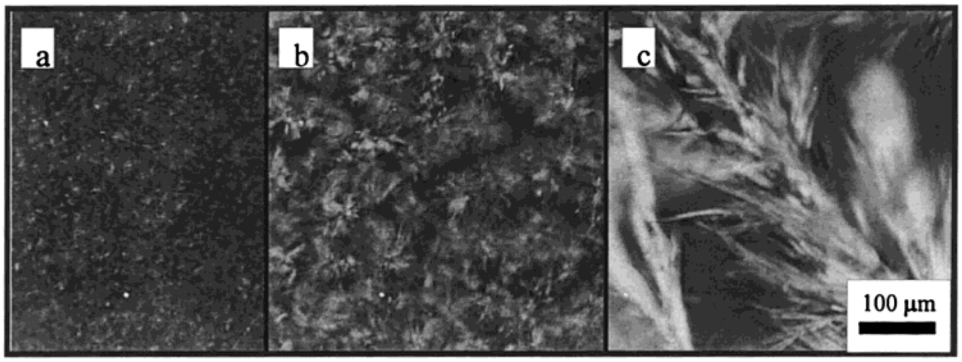

Figure 5. Optical micrographs (a, b, and c) at room temperature of 0.01 M (1.3 wt %) **18PI**/benzene gels prepared by fast (a), moderate (b), and slow (c) cooling (see text).

type of gelator anion and the ability of salts to gel an organic liquid could be discerned. We are unable to separate the several effects on gelation that accompany changing $\mathbf{X}^-$ of an $\boldsymbol{n}\mathbf{Y}^+$ cation.

In addition to their interest as micro-heterogeneous supramolecular assemblies, these gels may have several practical uses. Despite being less efficient than their ***n*NX** counterparts, ***n*PX** gelators may be more appropriate for many applications. Since they are more resistant to thermal decomposition, their gels can be recycled more times without a perceptible change of properties. Also, both series of ***n*YX** gelators do not absorb in the UV/vis region above 300 nm, and several of their gels do not scatter light appreciably. Especially the fast-cooled translucent gels with the **18YX** gelators should be useful for investigations of spectroscopic properties of partially immobilized solutes in the liquid component. As mentioned, both the ammonium and phosphonium based gels can be converted to “reverse aerogels”.[5] The structures, properties, and applications of these materials will the topic of future investigations.

Acknowledgment. We thank Allan Robertson of Cytec, Inc. for supplying the phosphines from which the ***n*PX** were synthesized and for several helpful discussions. D.J.A. is very grateful to the Achievement Rewards for College Scientists Foundation (ARCS) for a fellowship. The National Science Foundation is thanked for its support of this research.

CM990437+