

Pillaring of Layered Double Hydroxides with Polyoxometalates in Aqueous Solution without Use of Preswelling Agents

Jiandang Wang, Ying Tian, Ren-Chain Wang, and Abraham Clearfield*

Department of Chemistry, Texas A&M University, College Station, Texas 77843-3255

Received May 29, 1992. Revised Manuscript Received August 7, 1992

By using wet samples of layered double hydroxides (LDHs), the direct pillaring reactions of these compounds with polyoxometalate (POM) ions with Keggin-type structure have been effected in an aqueous one-step reaction without any organic preswelling agents. Full exchange of the Keggin ions into the layers is achieved as evidenced by X-ray powder diffraction, infrared spectroscopy, elemental analysis, and thermogravimetric analysis. The Mg-Al series of LDHs gave products consisting of a well crystalline phase with a *d* spacing of 14.7 Å and a less crystalline phase with a lower and less-defined interlayer distance. The Ni-containing LDHs, Ni₂Al(OH)₆NO₃ for example, yielded pillared products that correspond to the latter phase with interlayer spacings ranging between 11.0 and 13.5 Å. The lowered interlayer distance is attributed to creation of defects in the layers as a result of strong interactions between POM and the LDH layers. Surface area measurement results are also presented.

Introduction

In the search for catalysts that mimic the zeolite type structure but possess larger and more modifiable pores and active sites, new families of porous layered materials, known as PILCs (pillared inorganic layered compounds), have been synthesized by pillaring swelling clay minerals such as smectites.^{1,2} Their use as catalysts and sorbents is receiving considerable attention.³⁻⁵ Nonswelling layered compounds may also be pillared, but in such cases it is first necessary to expand the interlayer distance by intercalating an organic species into the interlamellar space of the compound before pillaring.^{6,7} This methodology has been applied to layered phosphates of groups 4 and 14.⁸ Both pillared smectite clays and pillared layered phosphates have negatively charged layers and positively charged pillars.

Layered double hydroxides (LDHs) constitute another class of layered compounds complementary to the clays in that they contain positively charged layers and anions in the interlamellar space.⁹ These hydrotalcite-like compounds may be represented by the general formula $M_n^{2+}M^{3+}(\text{OH})_{2n+2}(\text{X}^-)_n \cdot y\text{H}_2\text{O}$ where *n* may vary from 2 to 5 depending upon the particular combination of di- and trivalent elements, M²⁺ and M³⁺. The compounds have a brucite-like structure in which a fraction of the divalent ions are isomorphously replaced by trivalent ions imparting an excess positive charge to the layers. This charge is compensated by anions which reside in the interlamellar space.¹⁰ LDHs are readily synthesized by adding a mixture of the soluble di- and trivalent salts to sodium hydroxide and digesting the resultant precipitate to achieve crystallization. The interlayer spacings of the dried products range from 7.6 to 8.0 Å. A great variety of LDHs may be prepared in similar fashion, and there exists an extremely large number of stable isopoly- and heteropolyoxometalate (POM) anions^{11,12} which can potentially be used as pillaring agents. Therefore, one can envision a very large family of porous pillared materials which could be developed from such pillaring of LDHs. These pillared compounds would possess novel physical and catalytic properties that are manipulatable due to the wide variety of possible combinations of main-group and transition-metal elements in the layers as well as in the pillars.

Previously reported strategies to pillar LDHs have often involved pretreatment with organic reagents. Drezdron¹³ prepared the LDH in the presence of a large organic anion, preferably the terephthalate dianion, so as to intercalate it between the layers. An interlayer spacing of 14.4 Å was obtained by this procedure. In acid solution, subsequent exchange of [V₁₀O₂₈]⁶⁻ or [Mo₇O₂₄]⁶⁻ for the terephthalate anion was readily effected. Dimotakis and Pinnavaia¹⁴ heated Mg₃Al(OH)₈(CO₃)_{0.5}·2H₂O at 500 °C to convert the LDH to an oxide form. The latter was then reconstituted in water to form the layered double hydroxide with hydroxide ion as the interlamellar charge compensating anion. The addition of glycerol to the slurry resulted in extensive swelling of the LDH, and in this state large organic anions could be exchanged between the layers. The organic anions were in turn exchanged for polyoxometalate anions. In the study on one LDH, namely, Zn₂Al(OH)₆NO₃ prepared at high temperature, Kwon and Pinnavaia¹⁵ observed complete exchange with Keggin ions of negative 6 or 7 charge. Only partial exchange occurred with [PCuW₁₁O₃₉(H₂O)]⁵⁻, whereas lower charged Keggin ions did not exchange at all. They hence concluded that the exchange reaction depended upon both the charge and geometry of the incoming ion. For example, ions of low charge such as [PW₁₂O₄₀]³⁻ require more space than is available between the layers to completely replace the nitrate ion and mixing of large and small ions is apparently

(1) *Catalysis Today—Pillared Clays*; Burch, R., Ed.; Elsevier: Amsterdam, 1988; Vol. 2, pp 199-295.

(2) Vaughan, D. E. W. *Catal. Today* 1988, 2, 187.

(3) Reference 1, pp 297-355.

(4) Adams, J. M. *Appl. Clay Sci.* 1987, 2, 309.

(5) Figueras, F. *Catal. Rev. Sci. Eng.* 1988, 30, 457.

(6) Clearfield, A.; Roberts, B. D. *Inorg. Chem.* 1988, 27, 3237.

(7) Cheng, S.; Wang, T.-C. *Inorg. Chem.* 1989, 28, 1283.

(8) Maireles-Torres, P.; Olivera-Pastor, P.; Rodriguez-Castellon, E.; Jimenez-Lopez, A.; Alagna, L.; Tomlinson, A. A. G. *J. Mater. Chem.* 1991, 1, 739.

(9) Jones, W.; Chibwe, M. In *Pillared Layered Structures*; Mitchell, I. V., Ed.; Elsevier: London, 1990; pp 67-77.

(10) Allmann, R. *Chimia* 1970, 27, 4628.

(11) Pope, M. T. *Heteropoly and Isopoly Oxometalates*; Springer-Verlag: New York, 1983.

(12) (a) Domaille, P. J.; Watunya, G. *Inorg. Chem.* 1986, 25, 1239. (b) Smith, D. P.; Pope, M. T. *Inorg. Chem.* 1973, 12, 331. (c) Pope, M. T.; Varga, G. M., Jr. *Inorg. Chem.* 1960, 5, 1249. (d) Wu, H. J. *Biol. Chem.* 1920, 43, 189.

(13) Drezdron, M. A. *Inorg. Chem.* 1988, 27, 4628.

(14) Dimotakis, E. D.; Pinnavaia, T. J. *Inorg. Chem.* 1990, 29, 2393.

(15) Kwon, T.; Pinnavaia, T. J. *Chem. Mater.* 1989, 1, 381.

* To whom all correspondence should be addressed.

Table I. Effect of Wetness of LDH upon Extent of Pillaring Reactions with $[\text{PV}_3\text{W}_9\text{O}_{40}]^{6-}$

exp	LDH starting mater	treatment of LDH	reaction conditions	prod XPD ^a
1A	$\text{Mg}_2\text{Al}(\text{OH})_6\text{Cl}$, hard, dry solid	slurried for ~1 h	pH = 4, $T = 70^\circ\text{C}$, stirred 24 h	7.9 Å
1B	$\text{Mg}_2\text{Al}(\text{OH})_6\text{Cl}$, hard, dry solid	ground and slurried 24 h	pH = 4, room temp, stirred 24 h	11.4 Å + 7.8 Å (60%)
1C	$\text{Ni}_2\text{Al}(\text{OH})_6\text{NO}_3$, hard, 11% H_2O	not well ground, slurried ~3 h	pH = 4, room temp, stirred 24 h	11.4 Å + 7.8 Å (8%)
1D	$\text{Ni}_2\text{Al}(\text{OH})_6\text{NO}_3$, soft, 17.4% H_2O	well ground, slurried ~4 h	pH = 4, room temp, stirred 10 min	11.8 Å (100%)
1E	$\text{Ni}_5\text{Al}(\text{OH})_{12}\text{NO}_3$, dry solid	well ground, slurried 4 d	pH = 4, $T = 70^\circ\text{C}$, stirred 48 h	12.2 Å + 7.9 Å (65%)
1F	$\text{Ni}_5\text{Al}(\text{OH})_{12}\text{NO}_3$, wet solid, 70% H_2O	slurried 4.5 h	pH = 4, room temp, stirred 24 h	12.2 Å + 7.8 Å (15%)
1G	$\text{Mg}_2\text{Al}(\text{OH})_6\text{NO}_3$, wet solid, 60% H_2O	slurried 3 h	pH = 3.8, room temp, stirred 5 min	11.7 Å (100%)
1H	$\text{Mg}_5\text{Al}(\text{OH})_{12}\text{NO}_3$, dry solid	well ground and slurried 3.5 h	pH = 4, $T = 70^\circ\text{C}$, stirred 48 h	11.3 Å + 7.9 Å (20%)
1I	$\text{Mg}_5\text{Al}(\text{OH})_{12}\text{NO}_3$, wet solid, 60% H_2O	slurried 3 h	pH = 6.8, $T = 70^\circ\text{C}$, stirred 15 min	13.0 Å (100%)
1J	$\text{Zn}_2\text{Al}(\text{OH})_6\text{NO}_3$, wet solid, 80% H_2O	slurried 2 h	pH = 6.3, room temp, stirred 19 h	11.6 Å (100%)

^aThe (003) reflection, which is the lowest in 2θ and indexed as (003) based on the crystal structure, in X-ray powder diffraction patterns is given as representing the interlayer spacing. Number in parentheses indicates relative amount of the specified phase.

thermodynamically unfavorable. Woltermann¹⁶ interacted LDHs with isopoly and heteropoly POMs at 90°C to obtain some products with high surface area. His work, however, lacks characterization, and the surface area mostly resulted from exterior meso- and macropores.¹⁷

The above studies deal with individual examples of LDHs and involve more than one reaction step. Meanwhile, systematic research has been carried out in our laboratory to explore direct and general routes to synthesize polyoxometalate (POM) pillared layered double hydroxides under mild conditions.¹⁸ In contrast to earlier work, we have found that the ease of pillaring depends most directly upon the condition of swelling of the LDH, and pillaring can be effected in aqueous solution without assistance of any other agents. After the LDH had been soaked in deionized water for a sufficiently long period, the aqueous slurry was slowly added to a dilute solution of a Keggin ion salt and pillaring took place immediately.

Experimental Section

The preparation and pillaring reactions were performed under a prepurified nitrogen atmosphere by using Schlenk techniques.¹⁹ Deionized water was further purified to 18.3 MW cm in resistivity through a Barnstead NANOpure II system (Sybron) for the pillaring reactions and then freshly boiled and degassed before being used in LDH synthesis reactions. Salts of Keggin-type anions were synthesized by using literature procedures.¹² The pH values were measured with a Corning pH meter Model 220 fitted with a Fisher combination electrode. Reagents and other solvents were from commercial sources. X-ray powder diffraction patterns were obtained with a RU200 rotating anode Rigaku diffractometer using monochromatized $\text{Cu K}\alpha$ radiation. Infrared spectra were recorded on a Digilab FTS-40 spectrophotometer (Bio-Rad) on pressed KBr pellets under an N_2 atmosphere. Thermogravimetric analyses were performed with a DuPont 951 thermogravimetric analyzer at a typical heating rate of $5^\circ\text{C}/\text{min}$ under a nitrogen flow. Surface area and pore-size measurements were made on a Quantachrome AUTOSORB-6 sorption system. Metal analyses by neutron activation were performed at the Center for Chemical Characterization & Analysis in the Chemistry Department at Texas A&M University. C, H, N, and P analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

$\text{Ni}_5\text{Al}(\text{OH})_{12}\text{NO}_3 \cdot 3\text{H}_2\text{O}$. A mixture consisting of 73.20 g of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.25 mol) and 18.89 g of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.05 mol) in 300 mL of distilled, deionized water was added, together with a 2 N NaOH solution, to a large flask containing 150 mL of water. Rapid stirring was maintained throughout the addition, and relative rates of addition were such as to keep the pH at 10.0 ± 0.2 . After addition was complete, the temperature was maintained

at $75\text{--}80^\circ\text{C}$ for 16 h under a blanket of N_2 . The solid was then filtered under N_2 , washed with H_2O and Et_2O , and dried at 70°C for 24 h. The yield was 30.88 g or 96% of theoretical. Elemental analysis found Ni, 43.5%; Al, 4.46%; N, 2.40%; C, 0.36%; H, 2.95%. Calculated for $\text{Ni}_{4.5}\text{Al}(\text{OH})_{10.7}\text{NO}_3(\text{CO}_3)_{0.15} \cdot 3.4\text{H}_2\text{O}$: Ni, 43.63%; Al, 4.46%; N, 2.31%; C, 0.30%; H, 2.91%. The water content as determined by thermogravimetric analysis was 11.45%. X-ray d spacings: 7.9, 3.9, 2.6 Å. The infrared band at 1386 cm^{-1} is that from NO_3^- , and a small shoulder at 1360 cm^{-1} confirmed the presence of the small amount of carbonate ion. Other LDHs were prepared in a similar fashion with varied amounts of starting materials in the desired ratio.

$\text{Mg}_5\text{Al}(\text{OH})_{12}(\text{PV}_3\text{W}_9\text{O}_{40})_{1/6}$. A slurry of 1.67 g (4 mmol) of wet, freshly prepared $\text{Mg}_5\text{Al}(\text{OH})_{12}\text{NO}_3$ in 35 mL of distilled, carbonate-free water was stirred for 3 h to ensure complete wetness of the LDH. This slurry was added dropwise to a solution (pH 5.5) containing 3.65 g (1.3 mmol) of $\text{K}_6\text{PV}_3\text{W}_9\text{O}_{40}$ in 500 mL of H_2O at a temperature of 75°C . The reaction mixture was stirred for 24 h and then the orange-yellow precipitate was recovered by filtration, washed with four 100-mL portions of distilled, deionized water, and dried in air overnight. The yield was 2.45 g or 80%. Its X-ray diffraction pattern, TGA, infrared spectrum, and elemental analyses indicated that a pillared product had indeed been obtained. Anal. Found: Mg, 16.9%; Al, 3.41%; V, 3.31%; W, 36.0%. Calcd for $\text{Mg}_5\text{Al}(\text{OH})_{12}(\text{PV}_3\text{W}_9\text{O}_{40})_{1/6}$: Mg, 15.9%; Al, 3.52%; V, 3.33%; W, 36.0%. Other pillaring reactions were carried out in aqueous media under similar or improved conditions that are better described along with the obtained results in the next section.

Results and Discussion

The LDHs used in our study are the Mg_2Al to Mg_5Al series, Ni_2Al to Ni_5Al series, and Zn_2Al and Zn_3Al containing NO_3^- or Cl^- as the gallery anions. The nature of the anion initially present in the LDH has significant influence on the ion-exchange reaction. Thus, anions weakly held between the hydroxide layers are more appropriate for our purpose as they can easily be replaced by the pillaring anion. Our experience has shown that the order of preferred leaving anions is $\text{NO}_3^- > \text{Cl}^- > \text{SO}_4^{2-} > \text{CO}_3^{2-}$. Carbonate is the hardest to be exchanged out, and therefore we have vigorously avoided its formation by using degassed water and CO_2 -free atmosphere.¹⁹

Each of the LDH samples tends to have different properties, ranging from hard glassy particles to soft powders, depending upon the degree and method of drying. We first observed, in a qualitative manner, that the ease and completeness of pillaring could be correlated with the softness of the LDH powder and the length of time the LDH was slurried with water prior to the pillaring reactions. For example, the hard glassy particles did not pillar irrespective of the charge of the pillaring anion. However, partial pillaring could be effected upon vigorously grinding the glassy particles into a very fine powder and then stirring the powder in water, with heating, for an extended period. This trend is evident in Table I which summarizes pillaring reactions of several types of starting LDH with

(16) Woltermann, G. M. U.S. Patent 4,454,244, 1984.

(17) Pore-size distribution data are based on our reproduction of Woltermann's compounds since his patent, ref 15, disclosed only the total surface area values.

(18) Wang, J.; Tian, Y.; Wang, R.-C.; Colón, J.; Clearfield, A. *Mater. Res. Soc. Symp. Proc. Anaheim, CA*; Maroni, V. A., Ed.; Materials Research Society: Pittsburgh, PA, 1991; Vol. 233, pp 63-80.

(19) Shriver, D. F.; Drezdon, M. A. *The Manipulation of Air-Sensitive Compounds*, 2nd ed.; Wiley: New York, 1986.

Table II. Pillaring of Ni₂Al(OH)₆NO₃ with Different Keggin Ions

exp	Keggin ion salt	reaction conditions	prod XPD ^a
2A	Na ₃ PW ₁₂ O ₄₀	LDH slurried 22 h, added to solution of K.I. ^b at pH 2.0, room temp, stirred 5 min	11.2 Å (100%)
2B	K ₃ PV ₂ W ₁₀ O ₄₀	LDH slurried 3 h, added to K.I. solution at pH 3.5, room temp, stirred for 6 min	11.7 Å (100%)
2C	K ₃ PV ₃ W ₉ O ₄₀	LDH slurried 4 h, added to K.I. solution at pH 4.0, room temp, stirred 100 min	11.8 Å (100%)
2D	(NH ₄) ₆ HPV ₄ W ₈ O ₄₀	LDH slurried 24 h added to K.I. solution at pH < 4.0, room temp, stirred 1 h	11.9 Å (100%)

^aThe lowest 2θ reflection line, presumably (001), in X-ray powder diffraction patterns is given as representing the interlayer distance in the pillared product. Number in parentheses indicates relative amount of the specified phase. ^bK.I. = Keggin ion.

the Keggin ion [PV₃W₉O₄₀]⁶⁻. We have also experimented with a variety of other anions having the Keggin-type structure and discovered that the ease of pillaring becomes almost independent of the anion charge as long as the LDH was thoroughly wet. Table II contains our pillaring reaction results of one typical LDH with a series of Keggin ions. Since the Ni₂Al(OH)₆NO₃ used in this series was a wet sample and was further soaked for at least 3 h to ensure thorough wetness, complete conversion to a pillared phase (~11.8 Å) was observed with all the Keggin ions ranging from 3- to 7- in the anion charge.

Layered double hydroxides consist of metal hydroxide sheets (layers) which are positively charged because of the partial substitution of the divalent metal ions in the brucite structure by trivalent ions. This positive charge is balanced by anions within the interlamellar space. The space between the layers is not completely filled up with these charge balancing ions, allowing incorporation of water (or other polar molecules)²⁰ in the interlayer gallery spaces. The amount of water present in a sample of LDH is variable and nonstoichiometric and depends upon the drying procedure. For example, thermogravimetric analysis (TGA) experiments showed that a particular batch of Ni₂Al(OH)₆NO₃ contained more than 25% H₂O when air dried overnight, 17% after drying at 70 °C for 7 h, and less than 11% after drying at 70 °C for 24 h. The physical appearance of the solid changes according to its water content; thus, the sample with 11% H₂O was dark green, shiny, glassy, and hard, unlike the other two which were soft and light green in color. For convenience, we will hereinafter refer to LDH samples containing less than and more than 15% water as the hard and the soft LDHs, respectively. Moreover, we will use the term wet LDH to describe any LDH sample that is never separated from water after its preparation, i.e., filtered, washed but not dried, and stored with water. The wet samples usually contain at least 50 wt % of water and may contain as much as 90% by weight.

The amount of interlayer water also changes the magnitude of the interlayer spacing. For example in Ni₂Al(OH)₆NO₃, there is a steady increase from 7.8 Å for dried samples with less than 11% water to a value of ~9 Å at about 50% water content. Further increase of water content in separated samples did not seem to cause any increase in interlayer distance beyond 9.2 Å. However, samples that were freshly prepared and never separated from the mother liquor showed a *d* spacing of ~15 Å with absence of any other reflections up to 2θ = 20° (*d* = 4.44 Å). These observations suggest that, at least up to a certain water content, there is a gradual increase in the interlayer spacing to 9 Å with water uptake and then either a discontinuous change to a 15 Å spacing occurs or we have not detected the intermediate stages between 9 and 15 Å.²¹

It should be pointed out that all of the water may not necessarily reside between the layers. In fact, we have observed that in Mg-Al LDHs most of the H₂O is interlayer, whereas in the less crystalline samples of Ni-Al LDHs a larger portion of the H₂O is on the surface; it being unclear at the present whether this difference originates from the higher crystallinity or higher basicity of the Mg-Al type. Naturally, the *d* spacing is affected only by the interlayer H₂O and not by the surface H₂O.²² The swellability and its effects on intercalation reactions are well-known for a large number of clays.²³ Our study of the *d* spacing of wet, unpillared layered double hydroxides suggests that these compounds have swelling properties somewhat similar to the smectite clays and that readily swollen LDHs should undergo direct pillaring.

Despite scattered reports of success, direct pillaring of LDHs with Keggin-type polyoxometalates without assistance of pretreatment with organic intercalates has not previously been observed as a general route.¹³⁻¹⁶ Furthermore, our initial results of direct pillaring of LDH indicated that an intermediate intercalate in which the layers are spread apart would be necessary.²⁰ However, these initial reactions were all run with relatively hard, dry LDH samples. The subsequent discovery of the wettability and swelling of the LDH prompted us to reexamine the direct pillaring reaction with swollen samples. The present study shows that direct pillaring with polyoxometalates could easily be achieved as long as the LDHs are thoroughly wet. As summarized in Tables I and II, these experiments involve soaking of the well-ground or already wet LDH starting materials before adding them to the solution of a Keggin ion salt. A sufficiently long period of soaking is the key to successful pillaring. In some experiments, we ground the dry but "soft" LDH to a very fine powder which was then soaked in ample water until no solid would settle down when stirring was suspended. In other cases, we slurried the wet LDH for a few hours to ensure further wetness. The layers of LDHs apparently swell after either treatment and the pillaring reaction takes place readily in such slurries with swollen or open layers. The X-ray powder diffraction (XPD) data presented in Table I show that a much higher yield of the pillared product is obtained when the LDH is sufficiently wet (compare exp 1A with 1B, 1C with 1D, 1E with 1F, etc.).

The extent of the pillaring reactions is revealed not only by XPD but also by elemental analyses (Table III) and infrared spectra (Table IV) of the products. In the IR spectra, characteristic bands of the Keggin ions appear (with little shift in frequency) on top of the broad lattice vibration of the LDH (Figure 1). Meanwhile, the sharp NO₃⁻ group vibration at 1384 cm⁻¹ serves as a very sensitive diagnostic for the presence of any residual NO₃⁻ or any nitrate-containing starting materials. With these analytical tools, we studied the progression of the pillaring reactions. Table V lists our experiments in which products were

(20) Wang, R.-C.; Clearfield, A. Patent pending and manuscript in preparation.

(21) Among a series of XPD patterns collected during the process of slow air drying of a wet sample of highly crystalline Mg₂Al(OH)₆Cl, courtesy of W.-L. Shea, very sharp reflections were observed at both *d* = 15.0 and 9.0 Å on the first, wettest sample.

(22) Clearfield, A.; Kieke, M.; Kwan, J.; Colón, J. L.; Wang, R.-C. *J. Inclusion Phenom.* 1991, 11, 361.

(23) Theng, B. K. G. *The Chemistry of Clay-Organic Reactions*; Wiley: New York, 1974.

Table III. Elemental Composition of Pillared Layered Double Hydroxides

exp ^a		elemental analyses, %								
		Mg	Ni	Al	V	W	H	N	P	% H ₂ O by TGA
2A	found		16.9	4.50		44.6			0.70	5.4
	calcd ^a		16.83	4.55		44.66			0.63	3.04
2B	found		13.9	4.17	2.37	42.6				
	calcd ^b		13.7	3.94	2.38	43.0				7.89
2C = 1D	found		14.6	4.36	4.09	42.1	2.56		0.60	6.10
	calcd ^c		14.3	4.09	3.87	41.92	1.41		0.78	5.46
1G	found	11.6		4.92	5.02	42.0				4.1
	calcd ^d	10.5		4.65	3.95	42.8				
1I	found	16.9		3.41	3.31	36.0				
	calcd ^e	15.91		3.53	3.32	35.95				
2D	found		16.7	4.63	4.24	33.2				9.5
	calcd ^f		16.8	4.54	4.56	32.9				10.59

^a Calculated for Ni_{1.7}Al(OH)_{5.4}(PW₁₂O₄₀)_{0.12}(OH)_{0.64}·H₂O; F Wt = 592.77. ^b Calculated for Ni_{1.8}Al(OH)_{5.4}(PV₂W₁₀O₄₀)_{0.16}·3H₂O; F Wt = 684.60. ^c Calculated for Ni_{1.6}Al(OH)_{5.2}(PV₃W₉O₄₀)_{0.187}·2H₂O; F Wt = 659.22. ^d Calculated for Mg_{2.5}Al(OH)_{7.1}(PV₃W₉O₄₀)_{0.16}; F Wt = 580.22. ^e Calculated for Mg₅Al(OH)₁₂(PV₃W₉O₄₀)_{0.186}; F Wt = 764.01. ^f Calculated for Ni_{1.7}Al(OH)_{5.47}(PV₄W₈O₄₀)_{0.133}·3.5H₂O; F Wt = 594.81. ^g Experiment numbers refer to those used in Tables I and II.

Table IV. Characteristic Infrared Bands for Pillaring Reaction Products

exp ^a	formula	IR frequencies, cm ⁻¹	
2A	Ni ₂ Al(OH) ₆ (PW ₁₂ O ₄₀) _{1/3}	3423.8 (vs, br), 1621.4 (m), 1064.1 (m), 960.6 (m), 892.8 (w), 817.8 (vs), 727.0 (w), 670.4 (m, br)	
2B	Ni ₂ Al(OH) ₆ (PV ₂ W ₁₀ O ₄₀) _{0.2}	3417.8 (vs, br), 1620.3 (m), 1081.2 (m), 1056.7 (m), 959.0 (s), 883.6 (w), 799.8 (vs), 704.7 (vw), 633.9 (w)	
2C = 1D	Ni ₂ Al(OH) ₆ (PV ₃ W ₉ O ₄₀) _{1/6}	3432.3 (vs, br), 1621.5 (m), 1084.3 (m), 1055.3 (w), 960.0 (s), 877.1 (w), 798.1 (vs), 626.1 (m, br)	
1G	Mg ₂ Al(OH) ₆ (PV ₃ W ₉ O ₄₀) _{1/6}	3439.7 (vs, br), 1626.1 (m), 1086.9 (m), 1056.8 (w), 967.1 (s), 887.1 (w), 795.4 (vs), 665.5 (s, br)	
1I	Mg ₅ Al(OH) ₁₂ (PV ₃ W ₉ O ₄₀) _{1/6}	3525.7 (vs, br), 1629.5 (m), 1084.3 (m), 1054.2 (m), 959.9 (s), 833.6 (w), 808.2 (vs), 632.5 (s, br)	
1J	Zn ₂ Al(OH) ₆ (PV ₃ W ₉ O ₄₀) _{1/6}	3426.3 (vs, br), 1616.7 (m), 1461.9 (w), 1083.1 (m), 1054.2 (w), 854.5 (s), 804.6 (vs), 619.8 (s)	
2D	Ni ₂ Al(OH) ₆ (PV ₄ W ₈ O ₄₀) _{1/7}	3422.8 (vs, br), 1620.9 (m), 1089.7 (w), 1072.8 (m), 1051.3 (w), 956.7 (s), 871.2 (m), 785.3 (vs), 631.2 (m)	

^a The experiment numbers refer to those used in Tables I and II. vs = very strong, s = strong, m = medium, w = weak, vw = very weak, br = broad.

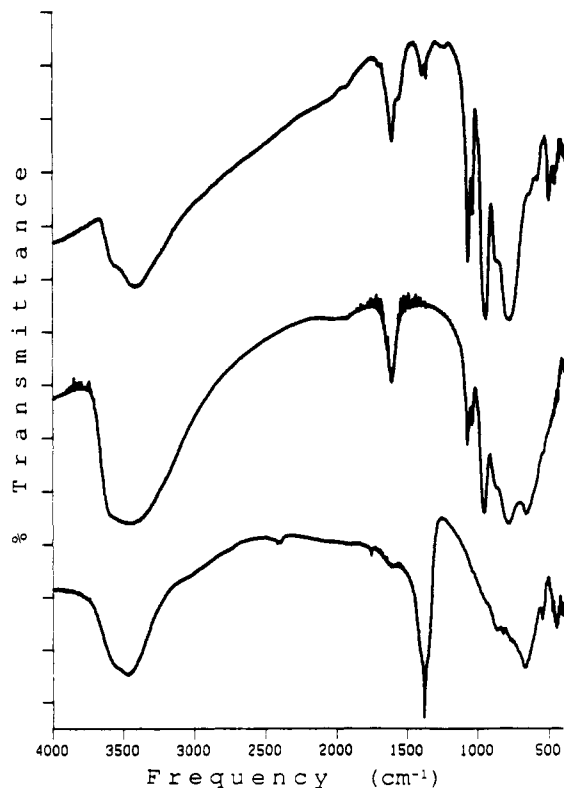


Figure 1. Infrared spectra of Mg₂Al(OH)₆NO₃ (bottom), K₆P-V₃W₉O₄₀ (top), and Mg₂Al(OH)₆(PV₃W₉O₄₀)_{1/6} (middle) obtained by the KBr disk method.

taken out and analyzed at different stages of the reaction. These clearly demonstrate that the reactions with completely wet LDHs reach 90% conversion to the pillared phase within 5–10 min. Also on the basis of IR and XPD data, we observed that all of the wet Mg–Al type LDHs

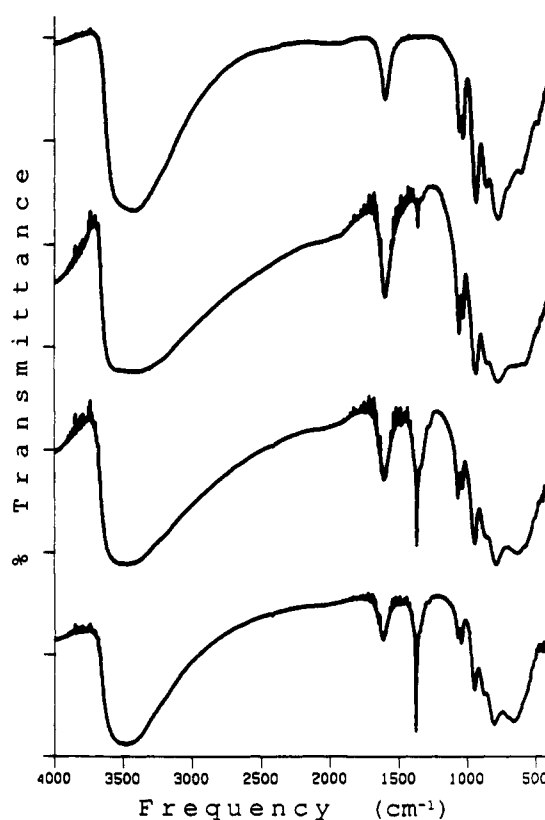


Figure 2. IR spectra for the products of the [PV₃W₉O₄₀]⁶⁻ pillaring reactions with (from top to bottom) Ni₂Al(OH)₆NO₃, Ni₃Al(OH)₆NO₃, Ni₄Al(OH)₁₀NO₃, and Ni₆Al(OH)₁₂NO₃ showing the decrease in Keggin ion uptake with increasing Ni:Al ratio.

pillar easily while the wet Ni–Al type shows a gradual decrease in completeness of the pillaring as the Ni to Al ratio increases from 2 to 5 (Figure 2). There are anom-

Table V. Progression of the Keggin Ion Pillaring Reactions

exp ^a and description	reaction time	elem anal. ^b		XPD intens ^c		IR intens ^d		est % of pillaring		
		M ²⁺ /Al	K.I./Al	prod	start M	NO ₃ ⁻	K.I.			
1D, Ni ₂ Al(OH) ₆ NO ₃ + K ₆ PV ₃ W ₉ O ₄₀	5 min	1.54	0.1657	898	10	11.27	99.91	99.5		
	65 min			899	~0	6.86	99.94	99.8		
	5 h			899	0	0.86	100	99.9		
	18 h			899	0	0.0	100	100		
1G, Mg ₂ Al(OH) ₆ NO ₃ + K ₆ PV ₃ W ₉ O ₄₀	5 min	1.50	0.1767	1077	5	0.83	99.87	99.7		
	20 h			564	0	0.39	100	99.9		
	46 h			2.62	0.180	536	0	0.0	100	100

^a Experiment numbers refer to those used in Table I. ^b K.I. = Keggin ion; K.I./Al = fraction of K.I. per Al estimated from analysis results of V, W vs those of Al, Ni, or Mg. ^c Prod = counts for the broad reflection at 11.5–13.0 Å (001) for the pillared LDH; start M = counts for the sharp reflection at 7.7–8.4 Å (001) for the unreacted LDH as starting material. ^d Relative infrared band intensities deduced from normalized percent transmittance for the NO₃⁻ vibration at 1384 cm⁻¹ and for one of the bands for the Keggin ion at ~799 cm⁻¹.

Table VI. Limiting Charge Values for Keggin Ion (K.I.) Pillars to LDHs

compound type ^a	layer charge density, e/Å ²	area per charge, Å ²	suitable K.I. charges ^b
M ₂ Al(OH) ₆ X	0.040	24.96	4- or more negative
M ₃ Al(OH) ₆ X	0.030	33.28	3- or more negative
M ₄ Al(OH) ₁₀ X	0.024	41.60	2- or more negative
M ₅ Al(OH) ₁₂ X	0.020	49.92	2- or more negative

^a M represents divalent metal ions, X interlayer anions. ^b On the basis of a calculation assuming 83 Å² for the area required for each Keggin ion.

alous occasions where Ni₅Al(OH)₁₂NO₃ was almost completely pillared, but conditions under which to reproduce the few successful experiments remain to be illuminated. Presumably, the inability of Ni–Al LDHs with Ni to Al ratios greater than 3 to pillar completely could be related to the previously mentioned observation that water molecules in Ni–Al compounds stay on the particle surface rather than between the layers. In contrast, the Mg–Al LDHs, whose water content is largely interlamellar, do pillar with greater ease.

There exists a large number of polyoxometalate ions with Keggin-type structure.¹¹ These isostructural anions represent a wide range of elemental compositions as well as negative charges. The presence of anion charges ranging from 3- to 8- enables us to study the effects of pillar charge on ease of the pillaring reactions and on properties of the pillared LDHs.

Since the pillaring of LDHs is based on ion-exchange reactions, the stoichiometry of the reaction will be determined by the charge of the anions, i.e., different molar amounts of Keggin ions with different negative charges will be exchanged for a certain LDH if the pillaring reactions go to completion. However, the Keggin ions we use as pillars are such bulky anions that spatial accommodation capacity has to be considered in addition to charge compensation (Table VI). For example, Ni₂Al(OH)₆NO₃ has a layer charge density of 0.04 e/Å², the highest in the present LDH series, which amounts to an area of 25.0 Å² per unit charge on the layer. Since an area of 83 Å² is needed to accommodate each of the Keggin ions with a 9.8-Å diameter in a triangular arrangement between the layers,^{15,18} the charge on the Keggin ions should be at least 4- in order to be capable of balancing the host layer charge, provided that the layers and Keggin ions both remain intact. In our experiments, as summarized in Table II, we managed to pillar Ni₂Al(OH)₆NO₃ not only with Keggin ions of 4- to 7- charges (exp 2B, 2C, 2D) but also with that of a 3- charge (exp 2A). The latter result is taken as partial evidence that alteration of the layers has occurred to decrease the "apparent layer charge density", which will be further discussed below.

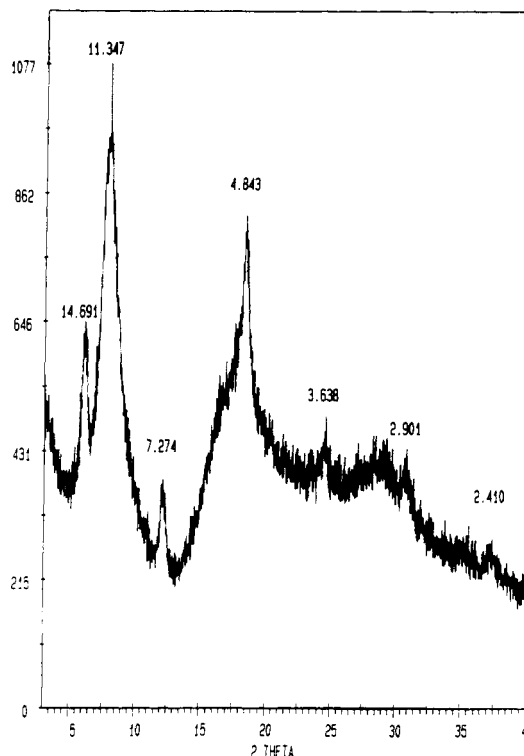


Figure 3. X-ray powder diffraction pattern for Mg₂Al(OH)₆-(PV₃W₉O₄₀)_{1/6}; numbers referring to *d*-spacing values in angstroms.

With an assumed gallery height of 9.8 Å for the Keggin ion and a layer thickness of ≈4.4 Å, the basal spacing should be at least 14.2 Å for the pillared LDH. In our experiments, however, the major products are found to have somewhat smaller *d* spacings. Pillaring of the Ni–Al LDHs, if completed, usually resulted in a product having only a single broad reflection which centers around *d* ≈ 12 Å. With the Mg–Al and Zn–Al LDHs two pillared products were present, judging from the X-ray powder diffraction. The major product shows a broad 11–13-Å reflection like the Ni–Al LDH and a minor product with reflections at 14.7, 7.35, 4.84, 3.63, 2.92, and 2.42 Å (Figure 3). The intensity of the 14.7-Å reflection is weak, and thus this peak is often "buried" under the very broad 11–13 Å peak for the major product. Nonetheless, the presence of the minor product phase can often be confirmed by the more prominent peaks at 7.35 and 4.84 Å. The observation of pillared products with smaller than the ideal *d* spacing, coupled with the fact that complete reaction with Keggin ions below the theoretically calculated charge limit took place indicated that interactions were occurring between the basic LDH layers and the somewhat acidic POM pillars.

We have observed that, when the pillaring reaction is carried out in acidic (pH 4–5) solution, the M²⁺/M³⁺ ratio

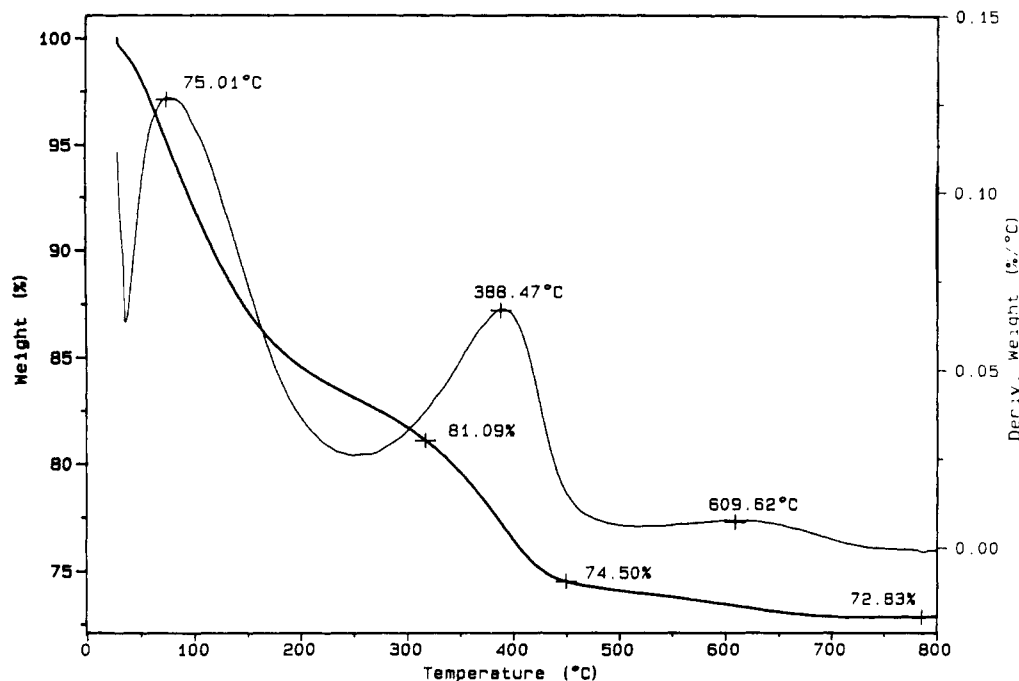


Figure 4. TGA and derivative curves of $\text{Ni}_{1.7}\text{Al}(\text{OH})_{5.4}(\text{PV}_3\text{W}_9\text{O}_{40})_{1/6} \cdot 5.5\text{H}_2\text{O}$. The two higher temperature weight losses, before and after 400 °C, respectively, are assigned to two different types of OH groups.

in the pillared product often becomes lower than that in the starting LDH (Table III), indicating partial dissolution of the divalent ion from the layers. It is conceivable that some OH groups are also removed along with the divalent metal ions and defects are created in the hydroxide layers during the pillaring reactions. Consequently, fitting of the Keggin ions into these "holes" would lead to basal spacing smaller than that expected for the pillared LDH without defective layers. Other evidence supporting the postulation of defects in the hydroxide layer includes observation of two distinguishable weight loss processes, one around 390 °C and the other above 500 °C, assignable to two different layer OH groups (Figure 4). Destruction of the polyoxometalate ions may also occur due to the basic environment in the interlayers and would result in a decreased d spacing. However, this is not likely the case, since no anomaly was obvious in the POM part of either the analyses or the IR spectra. In a previous study,¹⁸ we have examined computer graphic models for the interactions between the LDH layers and the POM pillars and, indeed, concluded that the interlayer distance is affected by the varying orientation of the Keggin ions and their penetration into the layers. Thus, when the Keggin ions are positioned in certain orientations and fit into the cavities created by layer dissolution, smaller d -spacing values are obtained which match the interlayer distances observed experimentally.

To distinguish these pillared defected layered structures from the so-called Woltermann's compounds,¹⁶ we compared our syntheses with his in a parallel fashion. We found that by Woltermann's method, LDHs were exposed to concentrated acidic POM solutions at elevated temperatures and thus most of the divalent metal ions were lost. For example, the Zn to Al ratio in one of the samples was reduced to 1:3. The products so obtained had very low and nonstoichiometric POM uptakes (0.015–0.02 mol per Al), unlike our products that showed regular stoichiometric or designed amounts of ion exchange. Moreover, X-ray diffraction revealed d spacings for Woltermann's compounds around 9.5 Å, substantially lower than our products.

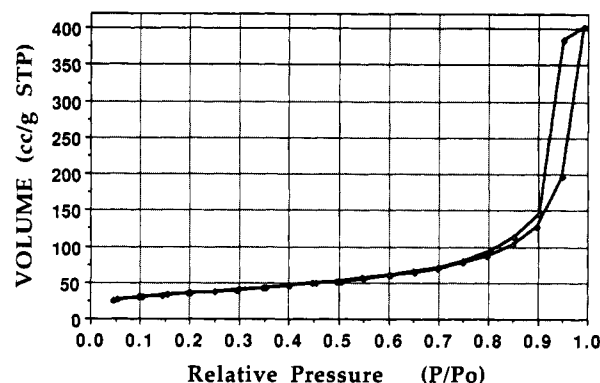


Figure 5. N_2 adsorption/desorption isotherm for a sample of $\text{Mg}_{3.5}\text{Al}(\text{OH})_{9.6}(\text{PV}_3\text{W}_9\text{O}_{40})_{0.067}$. Total BET surface area 136.5 m^2/g , mesopore area 124.1 m^2/g , MP method micropore area 22.16 m^2/g , average pore radius 85.3 Å.

N_2 adsorption experiments of our Keggin ion pillared LDHs prepared from room-temperature wet pillaring produced isotherms (Figure 5) closely resemble the B-type curves, indicating coexistence of micropores ($\omega < 20$ Å) and mesopores ($20 < \omega < 600$ Å).²⁴ BET surface area values of 136.5 and 134.4 m^2/g were obtained for samples approximating $\text{Mg}_{3.5}\text{Al}(\text{OH})_{9.34}(\text{PV}_3\text{W}_9\text{O}_{40})_{0.11}$ and $\text{Ni}_{1.5}\text{Al}(\text{OH})_{5.46}(\text{PV}_3\text{W}_9\text{O}_{40})_{0.09}$, respectively. The micropore volume to mesopore volume ratio was 1:9.3 for the former and 1:5.3 for the latter. This pore-size distribution is confirmed by scanning electron microscopy studies which revealed porous layered structures. The compounds made by Woltermann's methods gave higher surface area values but showed virtually no micropores. Therefore, pore-size distribution should be examined carefully when studying the surface properties of pillared layered materials as potential catalysts.

When samples of the Keggin ion pillared LDHs were subjected to repeated treatment with concentrated NH_4NO_3 or NaCl solution, the Keggin ions were partially ex-

(24) Gregg, S. J.; Sing, K. S. W. *Adsorption, Surface Area and Porosity*, 2nd ed.; Academic: New York, 1982.

changed out, as evidenced by the color, IR, XPD, etc. This observation is consistent with the proposed pillared layered structure and excludes the possibility that the product is the Keggin ion salt of the di- or trivalent cations from hydrolysis of the LDHs.

In summary, we have studied a complete range of reactions in aqueous media between the layered double hydroxides and the polyoxometalate anions of Keggin-type structure. The results demonstrate that Keggin ions with a variety of negative charge can be pillared into almost all kinds of layered double hydroxides, provided that the

latter are completely wet and the layers swollen with extended soaking. Full exchange of $[\text{PW}_{12}\text{O}_{40}]^{3-}$ into $\text{Ni}_2\text{-Al}(\text{OH})_6\text{NO}_3$ and $\text{Mg}_2\text{Al}(\text{OH})_6\text{NO}_3$ and the observation of broad X-ray diffraction peaks around 12 Å in the XPD are evidence that strong interactions take place between the Keggin ions and the LDH layers.

Acknowledgment. This research was supported in part by grants from the National Science Foundation (DMR-8801283) and the AMOCO Chemical Co. for which grateful acknowledgement is made.

Synthesis and Processing of Heterocyclic Polymers as Electronic, Optoelectronic, and Nonlinear Optical Materials. 1. New Conjugated Rigid-Rod Benzobisthiazole Polymers

John A. Osaheni and Samson A. Jenekhe*

Department of Chemical Engineering and Center for Photoinduced Charge Transfer,
University of Rochester, Rochester, New York 14627-0166

Received June 5, 1992. Revised Manuscript Received July 28, 1992

New conjugated rigid-rod polymers, poly(benzobisthiazole) (PBTT), poly(benzobisthiazole-2,6-diylvinylene) (PBTV), and poly(benzobisthiazole-2,6-diyldivinylene) (PBTDV), have been synthesized, and their structures and optical properties have been characterized, and they have been processed into thin films from their soluble coordination complexes. The molecular structure of the polymers was established by solution ^1H NMR spectra and infrared spectra of thin films or solid samples. The optical bandgap of the new polymers was in the range 2.07–2.34 eV, which is 0.14–0.41 eV smaller than the well-known nonlinear optical polymer poly(*p*-phenylenebenzobisthiazole) (PBZT). The solution processability and improved intrinsic electronic properties of the new polymers suggest that they have potential for electronic, optoelectronic, and nonlinear optical applications.

Introduction

The synthesis and processing of conjugated polymers as electronic, optoelectronic, and nonlinear optical materials are of current interest because of the envisioned application of such materials in various areas of technology.^{1,2} Ready processing of conjugated polymers to thin films or coatings is essential to their successful evaluation and use in these device applications. Although conjugated polymers are largely insoluble and intractible molecular materials, owing to their stiff chain structures and strong intermolecular interactions, significant progress is being made in developing new methods of solution processing of existing conjugated polymers. Most notable are the *soluble precursor*³ approach to polyacetylene^{3a} and vinylene-linked materials^{3b} such as poly(*p*-phenylenevinylene) and poly(thiophenevinylene) and the *soluble coordination complexes*⁴ approach to processing various heterocyclic and heteroaromatic conjugated polymers. It is therefore very important that processability and viable processing strategies be designed into the structures of new conjugated polymers. In this respect, new conjugated polymers containing heteroatoms are processable via their soluble coordination complexes.

The heterocyclic rigid-rod polybenzobisazole family, which includes poly(benzobisthiazoles), poly(benzobis-

oxazoles), and poly(benzimidazoles), has attracted much research interest in the past two decades because they exhibit high tensile strength, high modulus, and high thermal and environmental stability.⁴⁻⁹ The high strength

(1) (a) Brédas, J. L.; Chance, R. R., Eds. *Conjugated Polymeric Materials: Opportunity in Electronics, Optoelectronics, and Molecular Electronics*; Kluwer Academic Publishers: Dordrecht, Holland, 1990. (b) Marder, S. R.; Sohn, J. E.; Stucky, G. D., Eds. *Materials for Nonlinear Optics: Chemical Perspectives*; American Chemical Society: Washington, DC, 1991.

(2) (a) Osaheni, J. A.; Jenekhe, S. A.; Vanherzeele, H.; Meth, J. S. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* 1991, 32 (3), 154. (b) Yang, C. J.; Jenekhe, S. A.; Vanherzeele, H.; Meth, J. S. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* 1991, 32 (3), 165. (c) Osaheni, J. A.; Jenekhe, S. A.; Vanherzeele, H.; Meth, J. S.; Sun, Y.; MacDiarmid, A. G. *J. Phys. Chem.* 1992, 96, 2830. (d) Agrawal, A. K.; Jenekhe, S. A.; Vanherzeele, H.; Meth, J. S. *J. Phys. Chem.* 1992, 96, 2837. (e) Chen, W. C.; Jenekhe, S. A. *Macromolecules*, in press.

(3) (a) Edwards, J. H.; Feast, W. J. *Polym. Commun.* 1980, 21, 595. (b) Karasz, F. E.; Capistran, J. D.; Gagnon, D. R.; Lenz, R. W. *Mol. Cryst. Liq. Cryst.* 1989, 118, 327.

(4) (a) Jenekhe, S. A.; Johnson, P. O.; Agrawal, A. K. *Macromolecules* 1989, 22, 3216. (b) Jenekhe, S. A.; Johnson, P. O. *Macromolecules* 1990, 23, 4419–4429. (c) Yang, C. J.; Jenekhe, S. A. *Chem. Mater.* 1991, 3, 878–887. (d) Roberts, M. F.; Jenekhe, S. A. *Polym. Commun.* 1990, 31, 215. (e) Agrawal, A. K.; Jenekhe, S. A. *Chem. Mater.* 1992, 4, 95.

(5) (a) Wolfe, J. F.; Arnold, F. E. *Macromolecules* 1981, 14, 909. (b) Wolfe, J. F.; Loo, B. H.; Arnold, F. E. *Macromolecules* 1981, 14, 915.

(6) Wolfe, J. F. In *Encyclopaedia of Polymer Science and Engineering*; Wiley: New York, 1988; Vol. 11, 601–635, and references therein.

(7) Buckley, A.; Stuez, D. E.; Serad, G. A. In *Encyclopaedia of Polymer Science and Engineering*; Wiley: New York, 1988; Vol. 11, pp 572, and references therein.

* To whom correspondence should be addressed.