

Preparation and Characterization of Nanocomposites of Polyethers and Molybdenum Disulfide

John P. Lemmon and Michael M. Lerner*

Department of Chemistry and Center for Advanced Materials Research, Oregon State University, Corvallis, Oregon 97331-4003

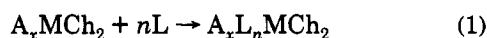
Received October 4, 1993. Revised Manuscript Received November 29, 1993*

Nanocomposites of poly(ethylene oxide) and molybdenum disulfide are prepared by the hydrolysis of lithiated molybdenum disulfide in an aqueous solution of PEO (mw 100 000) or poly[oxyethylene-oligo(oxyethylene)] (PEM, mw \approx 70 000). X-ray diffraction indicates an expansion of 8.3 Å in the interlayer spacing ($c \approx 14.5$ Å), consistent with the incorporation of a polymer double layer within the disulfide galleries. Reaction stoichiometries and elemental analyses indicate a composition of $\text{Li}_{0.12}(\text{PEO})_y\text{MoS}_2$ ($y = 1.0\text{--}1.3$) for the single-phase product. Analyses of extracted polymer demonstrate that high-molecular-weight polymer is present within the disulfide galleries. Scanning calorimetry of the nanocomposites indicates exothermic peaks at approximately 200 and 310 °C, which are demonstrated to be associated with an order/disorder phase transition and polymer decomposition, respectively. A fully amorphous, unstacked phase is irreversibly generated by heating the nanocomposites at 200 °C for several hours.

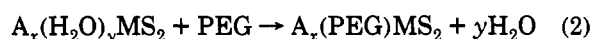
Introduction

The intercalation of organic compounds into layered transition metal dichalcogenides has been widely studied since the 1970s.^{1–8} Recent interest in the incorporation of polymers within inorganic hosts stems from the potential mechanical, structural, and electrical properties of organic/inorganic nanocomposites.^{9–12}

In general, layered ternary chalcogenides of the transition metals, A_xMCh_2 (A = alkali metal; M = Ti, Nb, Ta; Ch = S, Se, Te) spontaneously incorporate water or polar organic molecules to form stable compounds with solvated cations:



Exchange reactions can also be utilized to expand the chemistry of these materials. An example is the incorporation of the oligoether poly(ethylene glycol) by exchange of water in the hydrated lithium salt.⁵



A topotactic mechanism for the above reactions, in which the intersheet galleries expand or contract but the solid retains its two-dimensional character will be ineffective for the introduction of high-molecular-weight polymers due to the slow diffusion of macromolecules into the galleries.

One alternate route to polymer-containing nanocomposites involves the in situ polymerization of monomeric intercalants, and the preparation of materials such as poly(styrene)/ MoS_2 ,¹³ polyaniline/ V_2O_5 ,¹⁴ and polyaniline/ MoO_3 ¹⁵ have been reported by this method.

Murphy and co-workers⁴ and Schöllhorn and co-workers⁵ first observed that, under appropriate conditions, single-sheet colloids can be obtained by chemical oxidation of the lithiated metal disulfides. Morrison and co-workers^{13,16–18} and other groups¹⁹ have demonstrated that a colloidal suspension of single-sheet MoS_2 can incorporate molecular organics, organometallic complexes, or other complex cations when the single sheets are restacked. More recently, the incorporation of polyaniline into MoS_2 has been reported by this method.²⁰

We have previously reported the formation of nanocomposites of poly(ethylene oxide) and poly[oxyethylene-oligo(oxyethylene)] with MoS_2 ²¹ and here describe the preparation of single-phase materials and their characterization by X-ray powder diffraction, differential scanning calorimetry, thermogravimetric and elemental analyses, and electrical measurements.

Experimental Section

Li_xMoS_2 was prepared by the reaction of MoS_2 (Aldrich, 99% purity) with butyllithium (Aldrich, 1.6 M in hexane) using a

* Abstract published in *Advance ACS Abstracts*, January 15, 1994.

(1) Gamble, F. R.; DiSalvo, F. J.; Klemm, R. A.; Geballe, T. H. *Science* 1970, 168, 568.

(2) Gamble, F. R.; Osiecki, J. H.; DiSalvo, F. J. *J. Chem. Phys.* 1971, 55, 3525.

(3) Whittingham, M. S. *Mater. Res. Bull.* 1974, 9, 1681.

(4) Murphy, D. W.; Hull, G. W. *J. Chem. Phys.* 1975, 62, 973.

(5) Lerf, A.; Schöllhorn, R. *Inorg. Chem.* 1977, 11, 2950.

(6) Subba Rao, G. V.; Shafer, M. W. *Intercalated Layered Materials*; Levy, F., Ed.; D. Reidel: Holland, 1979; Vol. 6.

(7) *Intercalated Layered Materials*; Levy, F., Ed. D. Reidel: Boston, 1979.

(8) Schöllhorn, R. *Angew. Chem., Int. Engl. Ed.* 1980, 19, 983.

(9) Stucky, G. D. *Prog. Inorg. Chem.* 1992, 40, 99–177.

(10) Ozin, G. A. *Adv. Mater.* 1992, 4, 613.

(11) Stein, A.; Keller, S. W.; Mallouk, T. E. *Science* 1993, 259, 1558.

(12) Behrens, P. *Adv. Mater.* 1993, 5, 127.

(13) Divigalpitaya, W. M. R.; Frindt, R. F.; Morrison, S. R. *J. Mater. Res.* 1991, 6, 1103.

(14) Liu, Y. J.; DeGroot, D. C.; Schindler, J. L.; Kannewurf, C. R.; Kanatzidis, M. G. *J. Chem. Soc., Chem. Commun.* 1993, 593.

(15) Bissessur, R.; DeGroot, D.; Schindler, J.; Kannewurf, C.; Kanatzidis, M. J. *J. Chem. Soc., Chem. Commun.* 1993, 687.

(16) Divigalpitaya, W. M. R.; Frindt, R. F.; Morrison, S. R. *Science* 1989, 246, 369.

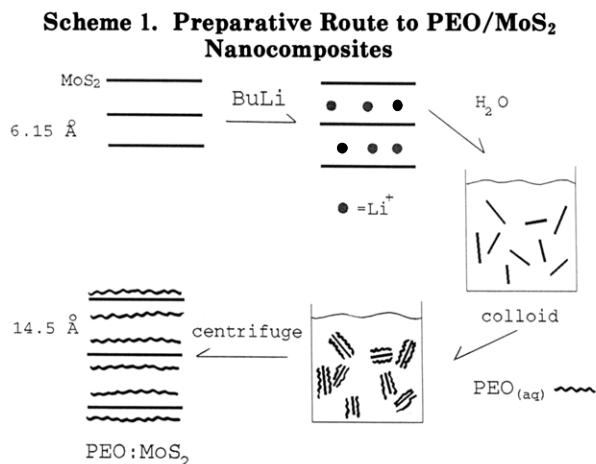
(17) Gee, M. A.; Frindt, R. F.; Joensen, P.; Morrison, S. R. *Mater. Res. Bull.* 1986, 21, 543.

(18) Miremadi, B. K.; Cowan, T.; Morrison, S. R. *J. Appl. Phys.* 1991, 69, 6373.

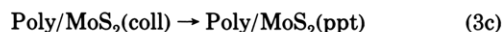
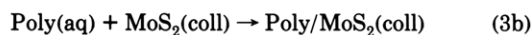
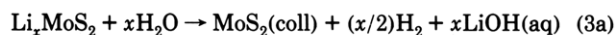
(19) Tagaya, H.; Hashimoto, T.; Karasu, M.; Izumi, T.; Chiba, K. *Chem. Soc. Jpn., Chem. Lett.* 1991, 2113.

(20) Kanatzidis, M. G.; Bissessur, R.; DeGroot, D. C.; Schindler, J. L.; Kannewurf, C. R. *J. Chem. Mater.* 1993, 5, 595.

(21) Lemmon, J. P.; Sloop, S. E.; Lerner, M. M. *Proc. Am. Chem. Soc., Inorg. Chem. Soc., Inorg. Chem.* 1993, Abstract No. 355.



literature method.²² Lithium analysis of the product by atomic absorption spectroscopy gives a stoichiometry of $\text{Li}_{1.15}\text{MoS}_2$. Poly(ethylene oxide) (PEO, Aldrich, mw = 100 000 Da) was used as received. Poly[oxymethylene-oligo(oxyethylene)] (PEM) was prepared as described previously.²³ The preparation of nanocomposites proceeds by exfoliation of the layered disulfide to form a stable colloid (3a), adsorption of polymer to these separated lamella (3b), and then restacking to form a layered nanocomposite (3c). Exfoliation of MoS_2 into single-sheet lamella was achieved



via the rapid hydrolysis and sonication of Li_xMoS_2 . Polymer/ MoS_2 nanocomposites (Scheme 1) were synthesized by the exfoliation of MoS_2 in deionized, deaerated (DI/DA) water containing a stoichiometric amount of polyether. Typical reactions involved 10–100 mg of PEO, 200 mg of Li_xMoS_2 , and a total water volume of 20 mL. The reaction stoichiometries were varied from 0.05–0.45 g of polymer/g of MoS_2 . The solutions were then neutralized with dilute acid; the solid product was separated by centrifugation at 13 000 rpm and washed several times with small amounts of DI/DA to ensure removal of LiOH and other soluble products. The nanocomposites were dried *in vacuo* at 70 °C for several hours, and subsequent manipulations were performed in a drybox or under dry nitrogen to exclude moisture and oxygen.

X-ray powder diffraction data were collected at ambient temperature on a Siemens D5000 powder diffractometer ($2^\circ < 2\theta < 30^\circ$, scan rate 0.002°). Pressed pellets of the reaction products were loaded into a holder modified to contain an inert atmosphere.

Simultaneous DTA/TGA data were obtained using a Netzsch, Inc. STA 419C thermal analyzer. Samples (20–25 mg) were loaded into aluminum pans, the sample chamber was evacuated and back-filled with He. Thermal scans from 50 to 400 °C were performed at 5 °C/min.

Lithium analysis utilized a Varian Techtron AA6 atomic absorption spectrophotometer at 670.8 nm with a sensitivity of 0.017 $\mu\text{g}/\text{mL}$. Polymer/ MoS_2 composites were analyzed following dissolution in hot, concentrated HNO_3 . Carbon and hydrogen analyses were performed by Desert Analytical (Tucson, AZ).

Gel permeation chromatography was performed on a Hewlett-Packard 1050 HPLC system using an ultrahydrogel linear column (Waters Chromatography) and Waters 410 RI detector. Samples were eluted at 0.85 mL/min in deionized water containing 0.05% NaN_3 .

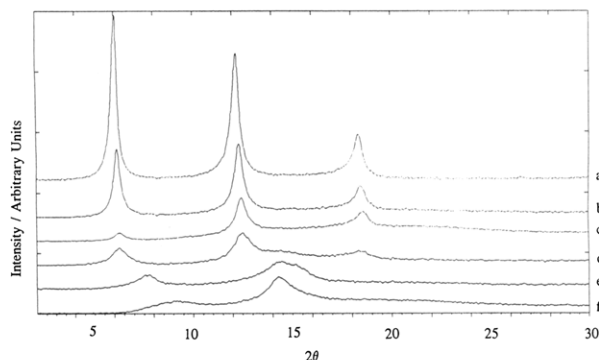


Figure 1. X-ray powder diffraction pattern of $\text{Li}_{0.12}\text{PEO}_x\text{MoS}_2$ prepared with reaction stoichiometries: (a) 0.45 g of polymer/g of MoS_2 , (b) 0.30 g/g, (c) 0.25, (d) 0.20, (e) 0.10, (f) 0.05.

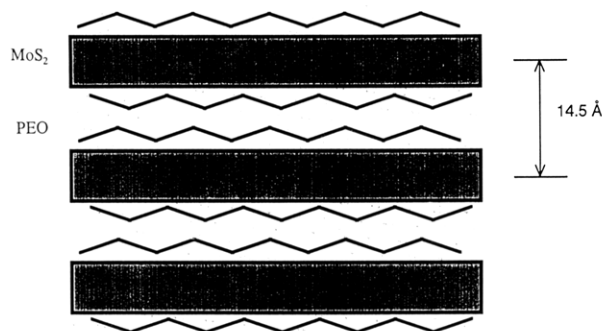


Figure 2. Arrangement of the double-layer nanocomposite structure.

Electrical conductivities between 77 and 274 K were determined using a four-probe method on pressed pellets maintained under a blanket of dry N_2 .

Results and Discussion

The powder diffraction data (Figure 1) for products of reactions *a–d* exhibit peaks near 6, 12, and 18°, corresponding to $d \approx 14.5$, 7.3, and 4.8 Å, which are indexed as the (001), (002) and (003) reflections for a nanocomposite phase. Preferred orientation in these pressed pellets reduces the intensity of all but (00 l) reflections. The *c*-repeat distances obtained increase slightly with higher polymer content (in *a*, 14.56(8) Å; *b*, 14.34(6); *c*, 14.21(12)), and the change in relative peak intensities is reproducible. The intensity changes are probably associated with different packing densities of the polymer layers in the nanocomposites (*vide infra*). Peak widths are similar for reaction products *a–c* and indicate stacking coherence lengths in the range of approximately 200–400 Å (20–25 repeat units). Reaction products *d* and *e*, prepared at lower polymer stoichiometries, show a broad peak associated with restacked MoS_2 . Similar diffraction data are obtained using PEM.

The distances between Mo planes observed in products *a–c* is 8.0–8.3 Å greater than in LiMoS_2 . This expansion is similar to that obtained by insertion of poly(ethylene glycol) into MS_2 ,⁵ oligo- or polyethers into montmorillonite,²⁴ and PEG or PEO into MPS_3 ,²⁵ and suggests that a polymer bilayer is incorporated into the intersheet region. A schematic structure of this arrangement is displayed in Figure 2. A greater expansion, indicating a phase containing more than a double layer of polymer, is not observed

(22) Murphy, D. W.; DiSalvo, F. J.; Hull, G. W.; Waszczak, J. V. *Inorg. Chem.* **1976**, *15*, 17.

(23) Lemmon, J. P.; Lerner, M. M. *Macromolecules* **1992**, *25*, 2907.

(24) Wu, J.; Lerner, M. M. *Chem. Mater.* **1993**, *5*, 835.

(25) Lagadic, I.; Léaustic, A.; Clément, R. *J. Chem. Soc., Chem. Commun.* **1992**, 1396.

Table 1. Elemental Analyses for C, H, and Li in PEO/MoS₂ Nanocomposites^a

expt	PEO/MoS ₂ (g/g)	Li wt %	C wt %	H wt %	H/C	composition
a	0.45	0.39	14.75	2.42	1.97	Li _{0.12} (PEO) _{1.34} MoS ₂
b	0.30	0.42	13.42	2.13	1.91	Li _{0.13} (PEO) _{1.18} MoS ₂
c	0.26	0.75	12.25	2.01	1.97	Li _{0.12} (PEO) _{1.05} MoS ₂

^a The representation (PEO)_n refers to *n* moles of the repeat unit (CH₂CH₂O).

in these reactions or other experiments utilizing a large excess of PEO. When the polymer stoichiometry is limiting, an ordered monolayer phase (with 4.0-Å expansion) can be obtained for the polyethers/montmorillonite nanocomposites;²⁴ however, an ordered product with this smaller expansion is not evident in these data. The weak, broad peak obtained at 0.10 g/g (Figure 1e) corresponding to a *c*-repeat distance of approximately 9.5 Å, might be ascribed to a poorly ordered monolayer phase. The broad peak near 14° at lower starting polymer stoichiometries (*d*-*f*) corresponds to the intersheet distance of restacked MoS₂.

The polymer conformation within the galleries cannot be determined directly from these diffraction studies, and a helical polymer conformation, as in crystalline PEO, cannot be excluded by steric arguments. Since the energy of polymer adsorption will decrease dramatically once monolayer coverage of the sheet surfaces is complete, a bilayer within the galleries (resulting from monolayer coverage of each sheet face) is a reasonable expectation from this exfoliation-adsorption method. In addition, indirect evidence strongly support the bilayer structure. This evidence includes the similar 8-Å expansion observed in a variety of small-molecule ethers in layered structures, the similar expansion observed for PEM (which is amorphous at ambient temperature), and the existence of an ordered 4-Å expanded phase in PEO/Na montmorillonite. The latter structure contains galleries that are too small to contain helical polymer chains, is prepared under similar conditions, and is related stoichiometrically to the bilayer phase.²⁴

Elemental analyses for C, H, and Li for reactions *a*-*c* are indicated in Table 1. The polymer/MoS₂ ratio found in the product depends on the mixing stoichiometries utilized in the nanocomposite syntheses. The large difference between initial and final stoichiometry in *a* indicates a threshold for polymer content (residual polymer is removed when the product is washed with water). The final polymer/MoS₂ ratios in *b* and *c* are slightly greater than the mixing stoichiometry; these results can be explained by the loss of a small amount of MoS₂ when the product is washed. The change in polymer content found for these products indicates a higher packing density of polymer within the disulfide galleries. This explanation is consistent with the reproducible change in relative peak intensities and slight increase in *c*-repeat distance with polymer content.

The Li content in the composites was analyzed, and the overall stoichiometry was determined to be close to Li_{0.12}(PEO)_xMoS₂ for all three samples. The lithium content most likely reflects a negative charge on MoS₂ sheets similar to that present in the hydrated lithium salts. Indeed, the lithium stoichiometry (*x* ≈ 0.1) is consistently similar to that obtained for hydrates prepared under similar conditions. Electrical measurements (Figure 5) indicate a semimetallic conductivity and thermal response,

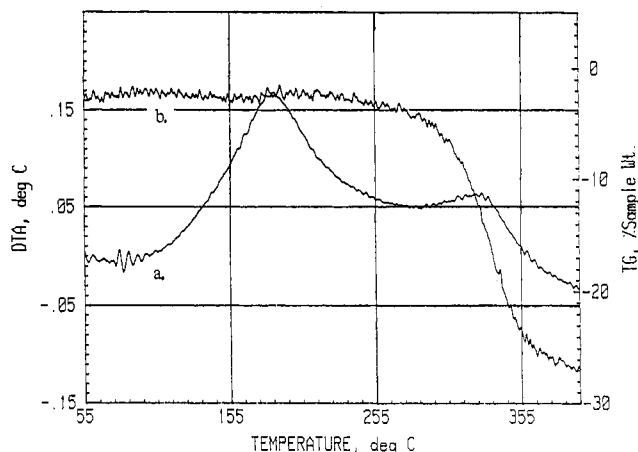


Figure 3. Simultaneous DTA/TGA scan obtained for Li_{0.12}PEO_{1.34}MoS₂: (a) DTA, (b) TGA.

which are again consistent with negatively charged MoS₂ layers.²⁶ Although Morrison *et al.* have suggested¹⁸ the presence of hydroxide in restacked MoS₂ to account for the negative charge associated with the MoS₂ layers, this explanation is inconsistent with our observations that similar colloids and restacked solids can be generated in polar organic solvents such as DMSO and DMF. The significant presence of LiOH is unlikely because our products have been washed with water, are not deliquescent, and display no unexplained diffraction peaks. Electrochemical studies to directly determine the charge state of the MoS₂ sheets within these nanocomposites are currently in progress.

A simultaneous DTA/TGA scan of the product from reaction *a* is presented in Figure 3. The absence of a melting endotherm at 60 °C indicates that no crystalline PEO phase occurs in the nanocomposite and illustrates again that the polymer conformation within these galleries is different than that of the bulk polymer. The exotherm near 310 °C arises from degradation of the polymer and the associated weight loss of 27 wt %, due to volatilization of the decomposition products, corresponds to the entire polymer content within the nanocomposite. X-ray diffraction of the nanocomposite after heating to 450 °C shows only a restacked MoS₂ phase. For comparison, the decomposition of pure PEO is observed at 360 °C in an inert atmosphere.

An additional exotherm between 125 and 255 °C is not associated with any significant sample weight loss. PEM/MoS₂ nanocomposites were also scanned and showed similar behavior. To further examine this transition, ambient-temperature X-ray diffraction pattern of a single pellet of the nanocomposite following heating at 200 °C in an Ar atmosphere for 3-6 h (Figure 4) were obtained and indicate an irreversible loss of sample order. After 6 h, the material appears entirely disordered. Subsequent heating of the pellet above 400 °C under inert conditions to remove the polymer component for several hours generates crystalline MoS₂. We conclude, therefore, that the disordered phase must contain MoS₂ sheets without

(26) Reports²⁷ have indicated the metallic nature of 1T-MoS₂, which can be prepared from single-sheet MoS₂. The uncharged sheets, however, are prepared only when an oxidant such as K₂Cr₂O₇ or I₂ was added to the suspension.

(27) Wypych, F.; Schöllhorn, R. *J. Chem. Soc., Chem. Commun.* **1992**, 1386.

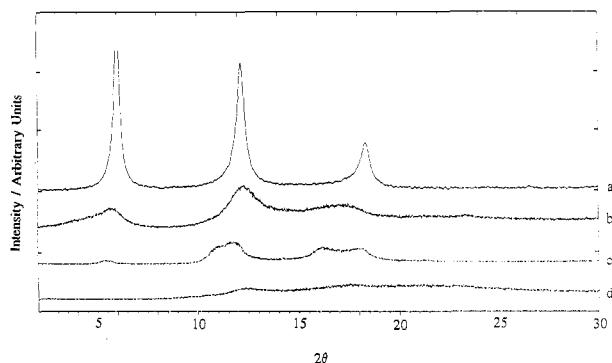


Figure 4. X-ray powder diffraction pattern for $\text{Li}_{0.12}\text{PEO}_{1.34}\text{MoS}_2$ heated to 200 °C: (a) 0 h; (b) 3 h; (c) 4.5 h; (d) 6 h.

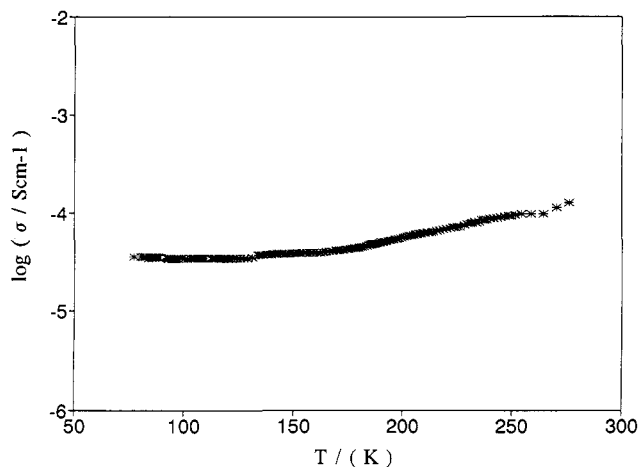


Figure 5. Electrical conductivity of $\text{Li}_{0.12}(\text{PEO})_{1.34}\text{MoS}_2$ nanocomposite.

a coherent stacking arrangement.²⁸ The generation of the disordered state requires a large rearrangement in the structure. The driving energy for this process may be provided by the thermally activated rearrangement of adsorbed polymer. The potentially high electroactive area for the disordered phase make it an attractive candidate for electrochemical applications. Experiments on the charge-discharge performance of these materials are currently underway.

GPC data on polymer extracted from the nanocomposites indicates that the polymeric component of these

(28) A structure consisting of a stacked arrangement of MoS_2 sheets of highly irregular intersheet spacing has also been suggested to the authors.

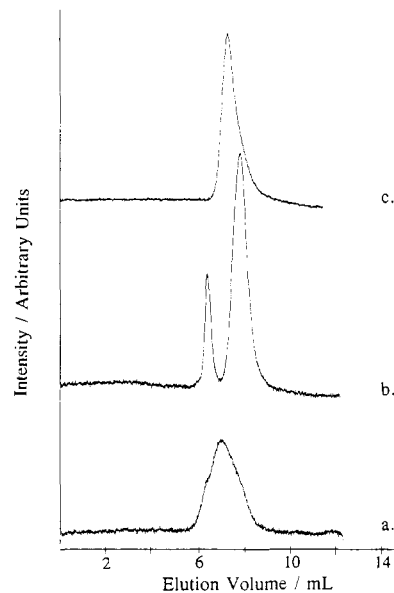


Figure 6. Gel permeation chromatography traces for (a) PEO starting reagent ($M_w \approx 100\,000$), (b) polymer extracted from $\text{Li}_{0.12}\text{PEO}_{1.34}\text{MoS}_2$, and (c) polymer extracted from $\text{Li}_{0.12}\text{PEO}_{1.34}\text{MoS}_2$ after heating at 200 °C. The calibration determined with PEO standards is $\log M_w = (-0.986 \times \text{elution volume}) + 11.974$.

materials is not degraded into low-molecular-weight fragments, although the results of crosslinking and scission are evident. Figure 6 shows that the extracted polymer from $\text{Li}_{0.12}\text{PEO}_{1.34}\text{MoS}_2$ contains significant molecular weight components centered at 450 000 and 20 000 Da. After heat treatment to form the unstacked nanocomposite, the extracted polymer has a single peak centered at 45 000 Da. In these samples, only 10–50% of the total polymer component can be extracted into an organic solution for analysis. Low-molecular-weight and other highly soluble products should be more readily desorbed from the disulfide surfaces, so the data obtained may not be representative of the entire polymer component. As no low-molecular-weight fragments are observed, however, the gross degradation of PEO does not occur. The details of polymer interaction with the disulfide lamella, and the mechanism of cross-link formation and bond cleavage, are of considerable interest and will be further explored by ^{13}C NMR studies on these solids.

Acknowledgment. The authors gratefully acknowledge supporting grants from the National Science Foundation (DMR-9157005) and AlliedSignal Inc.