lattice animals to describe crossover behavior in the Θ region, phase separation, and crossover behavior to isotropic single chains.

References and Notes

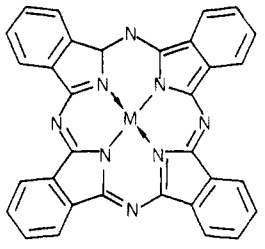
(1) M. Daoud, P. Pincus, W. H. Stockmayer, and T. Witten, *Macromolecules*, in press.
(2) S. Redner and Z. R. Yang, *J. Phys. A: Math Gen.*, **15**, L177 (1982), and references cited therein.
(3) S. Redner and A. Coniglio, *J. Phys. A: Math. Gen.*, **15**, L273 (1982).
(4) M. Daoud and J. F. Joanny, *J. Phys. (Orsay, Fr.)*, **42**, 1359 (1981).
(5) P.-G. de Gennes, "Scaling Concepts in Polymer Physics", Cornell University Press, Ithaca, NY, 1979.

Communications to the Editor

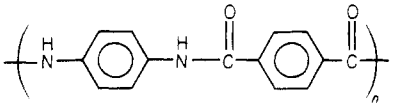
Processable, Oriented, Electrically Conductive Hybrid Molecular/Macromolecular Materials

Significant advances have recently been made in understanding and modifying the properties of electrically conductive molecular[1] and macromolecular solids.[1,2] Nevertheless, many of these substances exhibit limitations with regard to chemical/structural control at the molecular level, mechanical stability, air, water, and temperature stability, solubility and processability, and ease of synthesis. In the present communication, we address some of these limitations and describe an approach to the formation of a new class of hybrid molecular/macromolecular solids that can be spun into flexible, oriented, electrically conductive fibers.[3] The approach capitalizes upon similar solubility characteristics yet complementary electrical and structural properties of a well-characterized, chemically flexible, dopable "molecular metal" and a robust, processable, and in this case orientable, macromolecule. Although we illustrate with phthalocyanine molecular conductors[4,5] and a high-modulus "aramid" polymer,[6] the approach would appear to have considerable generality.

Metallophthalocyanines (A) and Kevlar[6] (B) are soluble



A



B

in strong acids. Partial oxidation of the former with a variety of electron acceptors results in highly conductive solids (e.g., Ni(Pc)I: σ(crystal) $\approx$ 500 Ω^{-1} cm^{-1}, σ(powder) $\approx$ 5 Ω^{-1} cm^{-1} at 300 K),[4,5] while the latter forms liquid crystalline solutions[6,7] which can be wet-spun[8] into strong, crystalline, highly oriented fibers.[6] Thus in a typical experiment, solutions of vacuum-sublimed phthalocyanine (e.g., Ni(Pc) and H_2(Pc), 5–18% by weight) and Kevlar-29 (3–7% by weight) were prepared in trifluoromethanesulfonic acid at 80 °C under an inert atmosphere. Fibers were then wet-spun from this viscous solution by extrusion under pressure[3,9] (through a stainless steel syringe needle) into an aqueous precipitation bath. Halogen oxidants[4] such as iodine can be introduced into the spinning solution prior to extrusion (presumably promoting more homogeneous doping) or into the precipitating bath (as I_3^-), or alternatively, the washed and dried fiber can be immersed in a benzene solution of I_2. In the latter two procedures, the extrudate is exposed to halogen for at least 24 h prior to washing and drying. Additionally, fibers can be doped electrochemically.[10] The resulting, darkly colored fibers are qualitatively strong and flexible[11] (decreasing flexibility with increasing M(Pc) content) and, as judged by appearance, mechanical properties, and transport properties (vide infra), are stable to air and moisture for many months. The composition of the fibers was established by elemental analysis.[12]

Table I
Electrical Conductivity Data for Hybrid Phthalocyanine/Keylar Fibers

composition[a]	σ_{RT},[b] Ω^{-1} cm^{-1}	act. energy,[c] eV
$[Ni(Pc)(K)_{4.36}I_{1.66}]_n$[d]	1.4	11.4×10^{-3}
$[Ni(Pc)(K)_{1.58}I_{1.27}]_n$[d]	1.8	6.6×10^{-3}
$[Ni(Pc)(K)_{0.67}I_{1.07}]_n$[d]	2.5	12.0×10^{-3}
$[Ni(Pc)(K)_{0.43}I_{1.56}]_n$[e]	4.7	17.2×10^{-3}
$[H_2(Pc)(K)_{0.54}I_{1.24}]_n$[d]	1.2	13.4×10^{-3}

[a] Pc = phthalocyaninato; K = Kevlar monomer unit = $-COC_6H_4CONHC_6H_4NH-$ (B). [b] Four-probe measurement; RT = 300 K. [c] From least-squares fit to the equation $\sigma = \sigma_0 e^{-\Delta/kT}$. [d] Doping in C_6H_6/I_2. [e] Doping in aqueous KI/I_2 followed by electrochemical oxidation (10 V, 3 h) in 0.8 M aqueous HI.

Electrical conductivity measurements were made by standard four-probe dc, techniques.[5a-c] Blocking electrode measurements established that ion conduction is not significant, while control studies (without M(Pc)) verified that the Kevlar host, which absorbed negligible halogen, is an insulator. M(Pc)/Kevlar fibers prepared without oxidation are also insulators. Charge transport data are compiled in Table I, and representative variable-temperature plots are shown in Figure 1A. The conductivity conforms approximately to thermally activated behavior, and phenomenological "activation energies" obtained by linear regression analysis of ln σ vs. $1/T$ plots are given in Table I. However, more satisfactory fits (especially at lower temperatures) are obtained to eq 1[5a,13] (Figure 1B), sug-

$$\sigma = \sigma_0 e^{-[T_1/(T+T_0)]} \quad (1)$$

gestive of transport involving inhomogeneous mixtures of metallike and nonconductive structural regimes with fluctuation-induced carrier tunneling between parabolic barriers separating the metallike regions.[5a,13] Maximum conductivities of the present fibers are on the order of ca. 5 Ω^{-1} cm^{-1}, which compares favorably with many conventional filled polymer composites.[14]

0024-9297/84/2217-0260$01.50/0 © 1984 American Chemical Society

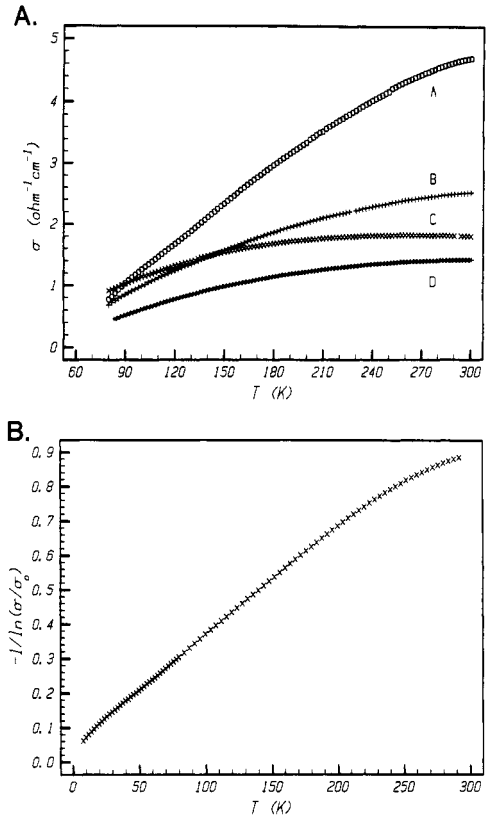


Figure 1. A. Variable-temperature four-probe electrical conductivity data for phthalocyanine/Kevlar hybrid fibers of composition (A) $[Ni(Pc)(K)_{0.43}I_{1.56}]_n$, (B) $[Ni(Pc)(K)_{0.67}I_{1.07}]_n$, (C) $[Ni(Pc)(K)_{1.58}I_{1.27}]_n$, (D) $[Ni(Pc)(K)_{4.36}I_{1.66}]_n$. K = Kevlar monomer unit **B**. B. Variable-temperature four-probe electrical conductivity data for a $[Ni(Pc)(K)_{0.85}I_{1.71}]_n$ fiber plotted according to the fluctuation-induced tunneling model of eq 1.

Efforts are presently under way to address the microstructurally important issues of whether these fibers consist of homogeneous solid solutions ("alloys") or whether (and to what degree) there is phase separation,[15] whether there is preferential orientation of M(Pc) subunits, and whether doping serves the same purpose as in molecular conductors (has oxidation of the M(Pc) units occurred?). Wide-angle X-ray diffraction studies have been conducted on single Kevlar/Ni(Pc)/I_2 fibers and on bundles using conventional photographic Laue and diffractometric techniques.[16] The superimposed diffraction patterns of Ni(Pc)I[5a] and Kevlar[6a,c,8b] are clearly evident. Moreover, all fiber stoichiometries reveal qualitatively significant preferential orientation[16,17] of the Kevlar chains and the Ni(Pc)I *c* (stacking) axis in the longitudinal fiber direction, as evidenced by "arcing" in the fiber photographs. Interestingly, the breadth of the Ni(Pc)I reflections suggests a high degree of imperfection or crystalline domains of dimensions $\lesssim$100 Å.[18] Resonance Raman spectra (spinning samples, ν_0 = 5145 Å) of the halogen-doped fibers exhibit the characteristic[4] scattering progression of I_3^- beginning at 108 cm^{-1} and phthalocyanine skeletal markers at 1600 and 1535 cm^{-1} diagnostic[19] of the phthalocyanine π cation radical. Clearly, the phthalocyanine moiety has been partially oxidized. Furthermore, Raman polarization[20] studies (e.g., Figure 2) indicate that the linear I_3^- units are preferentially oriented with the C_∞ axes aligned along the longitudinal fiber direction (consistent with the above diffraction results). For the data shown in Figure 2, analysis by a standard statistical formalism[21] yields $\langle \cos^2 \theta \rangle = 0.44$, where $\cos \theta$ is the direction cosine between the I_3^- C_∞ axis and the fiber axis. High-resolution solid-state ^{13}C CP-MAS NMR spectra are assignable in terms of superimposed

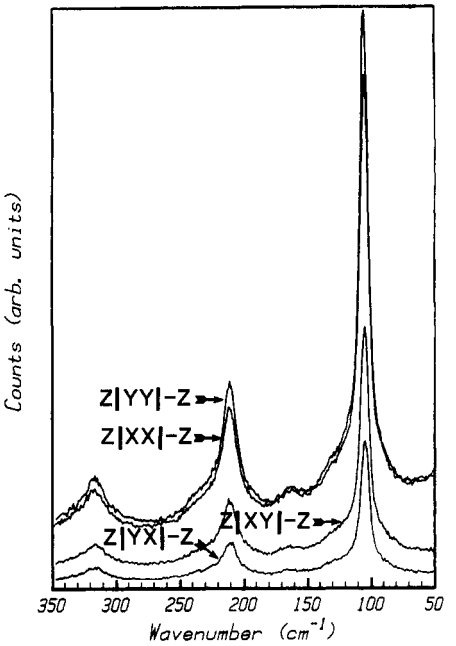


Figure 2. Polarized resonance Raman spectra (ν_0 = 5145 Å) of a bundle of $[Ni(Pc)(K)_{0.67}I_{1.07}]_n$ fibers. The I_3^- totally symmetric stretching fundamental is observed at 108 cm^{-1}. The Porto polarization symbols[20] give the polarization of the incident and sampled scattered radiation (in the $+Z$ and $-Z$ propagation directions, respectively). The fiber axis is in the *Y* direction.

aramid and partially oxidized Ni(Pc) resonances.[22]

In summary, these results show that a strategy of blending from solution well-characterized organic or metal–organic "molecular metals" with robust, processable, and orientable macromolecular hosts is a viable approach to the design of new, electrically conductive, processable, oriented organic solids. The present materials differ distinctly from simple filled polymer composites,[14] which do not begin with molecular building blocks and homogeneous solutions, are not rendered conductive by chemical or electrochemical doping (before or after processing), and are not generally orientable. The present materials also differ in obvious ways from recently reported air-sensitive composites prepared by acetylene polymerization within a polymer host[23] and from charge-transfer salt-filled films.[24] The latter materials in their present stage of development appear not to be as structurally well-defined, are far less conductive, are less amenable to varying doping methodologies, are not uniaxially oriented, and are apparently not suited for fiber formation.

Acknowledgment. This research was supported by the Office of Naval Research and by the NSF-MRL program through the Materials Research Center of Northwestern University (Grant DMR79-23573). We thank E. I. du Pont and Co. for samples of Kevlar-29, 3M Corp. for samples of triflic acid, and Professor S. H. Carr for stimulating discussions.

References and Notes

(1) (a) Miller, J. S., Ed. "Extended Linear Chain Compounds"; Plenum Press: New York, 1982; Vols. 1–3. (b) Epstein, A. J.; Conwell, E. M., Eds. "Proceedings of The International Conference on Low-Dimensional Conductors", Boulder, Colorado, August 9–14, 1981." *Mol. Cryst. Liq. Cryst.* 1981–1982, Parts A–F. (c) Alcăcer, L., Ed. "The Physics and Chemistry of Low-Dimensional Solids"; D. Reidel: Dordrecht, 1980. (d) Devreese, J. T.; Evrard, R. P.; van Doren, V. E., Eds. "Highly Conducting One-Dimensional Solids"; Plenum Press: New York, 1979.

(2) (a) Wynne, K. J.; Street, G. B. *Ind. Eng. Chem. Prod. Res. Dev.* **1982**, *21*, 23–28. (b) Etemad, S.; Heeger, A. J.; MacDiarmid,

A. G. *Annu. Rev. Phys. Chem.* **1982**, *33*, 443-469. (c) Baughman, R. H.; Brêdas, J. L.; Chance, R. R.; Elsenbaumer, R. L.; Shacklette, L. W. *Chem. Rev.* **1982**, *82*, 209-222. (d) Wegner, G. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 361-381. (e) Duke, C. G.; Gibson, H. W. In "Kirk-Othmer Encyclopedia of Chemical Technology"; Wiley: New York, 1982; Vol. 18, pp 755-793. (f) Seymour, R. B., Ed. *Polym. Sci. Technol.* **1981**, *15*.

(3) (a) Presented in part at the VI International Conference on the Chemistry of the Organic Solid State (Freiburg, West Germany, Oct 7, 1982) and the International Conference on Conducting Polymers (Les Arcs, France, Dec 14, 1982). (b) See also: Inabe, T.; Lyding, J. W.; Marks, T. J. *J. Chem. Soc., Chem. Commun.* **1983**, 1084-1085.

(4) Marks, T. J.; Kalina, D. W. In ref 1a, Vol. 1, pp 197-331.

(5) (a) Diel, B. N.; Inabe, T.; Lyding, J. W.; Schoch, K. F., Jr.; Kannewurf, C. R.; Marks, T. J. *J. Am. Chem. Soc.* **1983**, *105*, 1551-1567. (b) Dirk, C. W.; Inabe, T.; Schoch, K. F., Jr.; Marks, T. J. *Ibid.* **1983**, *105*, 1539-1550. (c) Inabe, T.; Lyding, J. W.; Moguel, M. K.; Kannewurf, C. R.; Marks, T. J. *Mol. Cryst. Liq. Cryst.* **1983**, *93*, 355-367. (d) Schramm, C. S.; Scaringe, R. P.; Stojakovic, D. R.; Hoffman, B. M.; Ibers, J. A.; Marks, T. J. *J. Am. Chem. Soc.* **1980**, *102*, 6702-6713. (e) Petersen, J. L.; Schramm, C. S.; Stojakovic, D. R.; Hoffman, B. M.; Marks, T. J. *Ibid.* **1977**, *99*, 286-288.

(6) (a) Schaefgen, J. R.; Bair, T.; Ballou, J. W.; Kwolek, S. L. K.; Morgan, P. W.; Panar, M.; Zimmerman, J. "Ultra-High Modulus Polymers"; In Cifferi, A., Ward, I. M., Eds.; Applied Science Publishers: London, 1979; pp 173-201. (b) Magat, E. E.; Morrison, R. E. *CHEMTECH* **1976**, *6*, 702-709. (c) Carter, G. B.; Schenk, V. T. J. In "Structure and Properties of Oriented Polymers", Ward, I. M., Ed.; Wiley: New York, 1976; Chapter 13. (d) J. Preson *Polym. Sci. Eng.* **1975**, *15*, 199-206.

(7) (a) Flory, P. J. *Proc. R. Soc. London* **1956**, *234*, 73-89. (b) Flory, P. J. *J. Polym. Sci.* **1961**, *49*, 105-128.

(8) (a) Cifferi, A.; Valenti, B., in ref 6a, pp 203-226. (b) Hancock, T. A.; Spruiell, J. E.; White, J. L. *J. Appl. Polym. Sci.* **1977**, *21*, 1227-1247.

(9) A Teflon-lined, anaerobic version of Stille's "sodium press" apparatus was employed: Sybert, P. D.; Beever, W. H.; Stille, J. K. *Macromolecules* **1981**, *14*, 493-502.

(10) (a) Inabe, T.; Marks, T. J., manuscript in preparation. Anodic methodology similar to that reported elsewhere[2,10b] was employed. (b) Nigrey, P. J.; MacInnes, D., Jr.; Nairns, D. P.; MacDiarmid, A. G.; Heeger, A. J. *J. Electrochem. Soc.* **1981**, *128*, 1651-1654 and references therein.

(11) Quantitative studies of mechanical properties are in progress.

(12) Traces of sulfur (<0.5%) are also detected in the analyses and may represent included CF_3SO_3H or $CF_3SO_3^-$ counterions.

(13) (a) Sheng, P. *Phys. Rev. B* **1980**, *21*, 2180-2195. (b) Park, J.-W.; Heeger, A. J.; Druy, M. A.; MacDiarmid, A. G. *J. Chem. Phys.* **1980**, *73*, 946-957.

(14) (a) Bigg, D. M.; Bradbury, E. J., in ref 2f, pp 23-38, and references therein. (b) Davenport, D. E., in ref 2f, pp 39-47, and references therein.

(15) Karasz, F.; MacKnight, W. J. In "Contemporary Topics in Polymer Science"; Pearce, E. M., Schaefgen, J.R., Eds.; Plenum Press: New York, 1977; Vol 2, pp 143-155 and references therein.

(16) (a) Tadokoro, H. "Structure of Crystalline Polymers"; Wiley-Interscience: New York, 1979; Chapt 4. (b) Spruiell, J. E.; Clark, E. S. *Methods. Exp. Phys.* **1980**, *16B*, 39-98. (c) Stein, R. S.; Wilkes, G. L., in ref 6c, Chapter 3.

(17) A more quantitative analysis is in progress.

(18) (a) Estimated from the Scherer equation.[5a,18b] (b) Klug, H. P.; Alexander, L. E. "X-ray Diffraction Procedures for Polycrystalline and Amorphous Materials"; Wiley-Interscience: New York, 1974; Chapter 9.

(19) Lomax, J. F.; Moguel, M. K.; Marks, T. J., unpublished results.

(20) Shepherd, I. W. *Adv. Infrared Raman Spectrosc.* **1977**, *3*, 127-166 and references therein.

(21) (a) Jen, S.; Clark, N. A.; Pershan, P. S.; Priestley, E. B. *Phys. Rev. Lett.* **1973**, *31*, 1552-1556. (b) Priestly, E. B.; Pershan, P. S. *Mol. Cryst. Liq. Cryst.* **1973**, *23*, 364-373.

(22) Toscano, P. J.; Marks, T. J., unpublished results.

(23) (a) Lee, K. I.; Jopson, H. *Makromol. Chem., Rapid Commun.* **1983**, *4*, 375-378. (b) Galvin, M. E.; Wnek, G. E. *J. Polym. Sci., Polym. Chem. Ed.* **1983**, *21*, 2727-2737.

(24) (a) Jeszka, J. K.; Ulanski, J.; Kryszewski, M. *Nature (London)* **1981**, *289*, 390-391. (b) Kim, O.-K. *J. Polym. Sci., Polym. Lett. Ed.* **1983**, *21*, 575-581.

(25) IBM Postdoctoral Fellow.

Tamotsu Inabe, Joseph F. Lomax, and Tobin J. Marks*

Department of Chemistry and the Materials Research Center Northwestern University, Evanston, Illinois 60201

Joseph W. Lyding[25] and Carl R. Kannewurf

Department of Electrical Engineering and Computer Science, and the Materials Research Center Northwestern University, Evanston, Illinois 60201

Kenneth J. Wynne

Chemistry Program, Office of Naval Research Arlington, Virginia 22217

Received May 23, 1983

The 4-Å Ruler, Using Exciplex Fluorescence To Study Small-Molecule Diffusion into Nonaqueous Dispersions of Polymer Colloids

The kinetics of small-molecule penetration into dispersions of colloidal polymer particles is commonly determined by weight uptake[1] or by particle swelling.[2] Other methods such as radiolabeling are possible. These methods share in common the fact that they determine the gross features of the uptake process. In this paper we pose the question of whether one could unveil details of the diffusion process with techniques capable of ca. 5-Å resolution. One might imagine complexities in the diffusion of small molecules into multicomponent particles, particularly sterically stabilized dispersions composed of two linked but mutually incompatible polymers.

Fluorescence techniques, particularly fluorescence quenching interactions, provide high-resolution methods for studying diffusion processes. If one were to prepare polymer particles containing small amounts of a fluorescent dye covalently bound to one particular polymer phase, one could use fluorescence quenching techniques to study the rate of penetration of small molecules with quenching capabilities into that phase.

The kind of information one gets depends upon the choice of chromophore and the nature of the quenching process. Consequently, fluorescence studies of different pairs of interacting groups could provide complementary descriptions of the detailed mechanism of the diffusion process.

As a prototype system, we chose poly(methyl methacrylate) (PMMA) particles sterically stabilized by polyisobutylene (PIB) dispersed in various alkane solvents. In our first experiments[3,4] we examined 2-μm-diameter particles covalently labeled with naphthalene (N) groups in the PMMA chains. Fluorescence energy-transfer experiments were carried out in which we measured the rate of energy transfer from the N* groups in the particle core to anthracene (A) molecules dissolved in the isooctane medium.[3] We learned that A penetrates quickly into the particles (less than 30 min) and that energy transfer from N* to A seems to occur with equal probability from all or most of the excited N groups.

These conclusions were based upon fluorescence decay measurements in which we found that varying the concentration of A in isooctane from 1×10^{-3} to 5×10^{-3} M increased linearly the decay rate of the naphthalene chromophores. A diffusion model permitted the diffusion constant of A in the particle to be calculated. Its value of 2×10^{-6} cm^2 s^{-1} is 8–10 orders of magnitude too large

0024-9297/84/2217-0262$01.50/0 © 1984 American Chemical Society