extraction of the swollen gels in tetrahydrofuran (see Scheme I).

Irradiation of 1 induces side-group coupling reactions to form a stable, cross-linked polymer matrix. The presence of cross-links was apparent from the swelling behavior and failure of the polymer to dissolve in tetrahydrofuran or water. The effect of the cross-linking was further evidenced in the ^{1}H and ^{13}C NMR spectra (see Figure 1). The broadening of the peaks, compared to those in the non-cross-linked polymer 1, was indicative of a decrease in side-group mobility.[13] A probable mechanism for cross-linking involves photolytic cleavage of C–H bonds followed by carbon radical recombination.[14]

It was also found that ultraviolet cross-linking of 1 was possible even in the absence of a photoinitiator and that this reaction was not dependent on the type of solvent (see Scheme I). The degree of cross-linking was found qualitatively to be greater for a given exposure time when benzophenone was utilized.[15] However, a cross-linking process that does not involve the addition of a photoinitiator has obvious advantages if the system is to be used for conductivity experiments. Previous studies have demonstrated that cross-linking of polymer 1 provides increased dimensional stability without reducing the ionic conductivity.[6,7]

Due to the similarity of the substituents in polymer 1 to the backbone structure of poly(ethylene oxide), films of the latter polymer were also investigated. Films of poly(ethylene oxide) were also shown to undergo cross-linking both in the presence and absence of benzophenone.[16]

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(13) Further evidence for the decrease in side-group mobility was given by the increase in the measured glass transition temperature for the cross-linked polymer 1: $T_g = -77.4$ °C.

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(15) Samples of polymer 1 with and without benzophenone present were irradiated with the ultraviolet source for 20 min. However, the films cross-linked without a photoinitiator present swelled more in THF or water than the gels formed in the presence of benzophenone. This indicates a lower rate of cross-linking in the absence of a photoinitiator.

(16) Films of poly(ethylene oxide) were cast onto glass slides (a) in the absence of benzophenone from H_2O and (b) with 10 mol % photoinitiator, from solutions in $CHCl_3$ or THF. Following solvent evaporation the polymer-coated glass slides were placed in quartz reaction tubes, which were purged with argon, sealed, and irradiated for 20 min with a 450-W Hg lamp. The cross-linked films were then immersed in H_2O to form solvent swollen gels.

A Conductive, Anisotropic Polymer Film Formed by Electroprecipitation of π-Stacks of an Imide Anion Radical and a Polycation

Chuan-Jian Zhong,† Baruch Zinger,† Vince Cammarata,† Paul H. Kasai,‡ and Larry L. Miller*,†

Department of Chemistry, University of Minnesota
Minneapolis, Minnesota 55455
IBM Almaden Laboratories, 650 Harry Road
San Jose, California 95120

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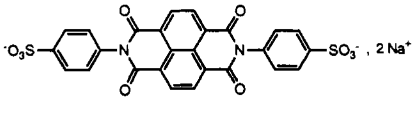
It has recently been shown that the anion radical of disulfonate salt 1 aggregates into π-stacks in aqueous salt solutions.[1] Described here are studies that demonstrate that this solution-phase aggregation can be enhanced by small amounts of cationic polymers, e.g., 2^+, and that it is possible to electroprecipitate thin films composed of $1^-/2^+$. Spectroscopic studies show that these air-stable films are somewhat anisotropic with stacks of 1^- anion radicals running preferentially along the plane of the thin film. Because of this structure the electrical conductivity is much higher along the film than across the thin dimension. These films have the further unusual property that the conductivity increases by 10^3 as the relative humidity changes from 0 to 90%. Close analogues of this material are conductive films composed of TCNQ$^-$ and cationic polymers.[2] These TCNQ$^-$ films are, however, isotropic and decomposed by moisture. Nonpolymeric, but anisotropic, films of 1 have been prepared by using the Langmuir–Blodgett method,[3] as have conducting LB films containing TCNQ$^-$.[4]



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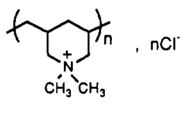

2^+

To study the aggregation in solution, aqueous solutions of 1^- (1–5 mM) were formed by reduction of 1 with sodium dithionite. As previously demonstrated,[1] these solutions are composed primarily of π-dimers, which have an absorption maximum at 1140 nm. Addition of an amount of polymer 2^+ sufficient to balance the charge on the trianion 1^- led to a spectrum with a near-infrared absorption maximum at 1700 nm. This band is characteristic of π-stacks.[1,5] Thus, the cationic polymer provided a template to organize the dimers into stacks in solution. We know of no previous example of this phenomenon.

Although it was possible to precipitate the salt $1^-,2^+$ as a black solid[1,6] a more interesting result was obtained by electroprecipitation.[7] Thus an aqueous solution of 1 (1 mM), with 2^+Cl^- (0.1 M) present as the supporting electrolyte, was reduced at a platinum electrode. The potential was held at –0.2 V vs SCE. Over a period of many minutes the current held steady at 0.01 mA cm^{-2}, and a shiny film grew on the surface. When thin, the film was brown; when thicker, it was black. After drying in vacuum, films 10–50 μm thick could be peeled off of the electrode. They were stable in air for more than 1 month. XPS analysis confirmed the elemental composition to be consistent with the structure $1^-,2^+$, with substantial chloride but only traces of sodium.

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† University of Minnesota.

‡ IBM Almaden Laboratories.

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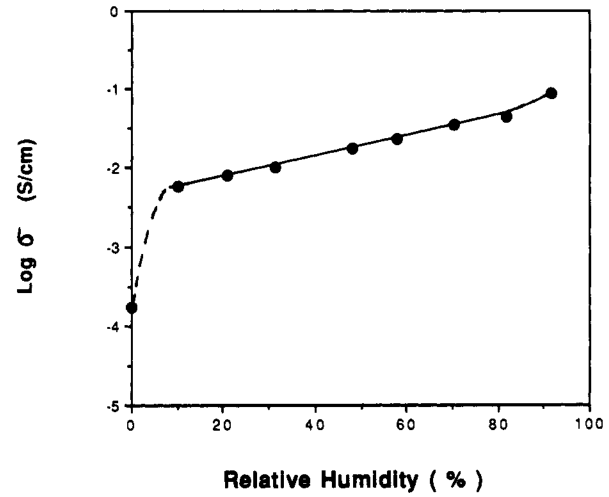

Figure 1. Conductivity of $1^-,2^+$.

Four-point-probe conductivity measurements were made on free-standing films with typical dimensions x = 1 cm, y = 1 mm, z = 20 μm, at room temperature in a controlled-humidity environment. Either using a standard four-point probe apparatus or attaching four wires to the sample with silver paste gave similar steady-state values for the x,y conductivity along the film. At 90% relative humidity this value was 0.1 S cm^{-1} and did not change after passage of 10 μA of current through the film for 1 h. The charge passed during this time is sufficient to electrolyze most of the ions in the film, and since the voltage did not increase, we conclude that the steady-state current is due to electronic and not ionic conduction. Conductivity across the thin dimension of the film was measured by attaching wires on each side with silver paste and had a value of about 10^{-7} S cm^{-1}. Thus, the conductivity is quite anisotropic.[8]

Figure 1 shows that the in-plane conductivity increases by 10^3 when the relative humidity is increased from 0 to 90%. Although it is not surprising that the film takes up water from the atmosphere, it is interesting that hydration improves the conductivity, which is electronic, so dramatically.

The structural anisotropy was demonstrated by ESR spectroscopy (Figure 2). When the x–y plane of the film was placed parallel to the applied field, an inhomogeneously broadened signal was observed. The inhomogeneity was that consistent with an ensemble of g values ranging from 2.0023 (free spin value) to 2.0044. When the sample was placed perpendicular to the field, the signal appeared isotropic at g = 2.0044. These observations are consistent with a film structure in which the stacks are preferentially oriented toward the x–y plane.[3,9]

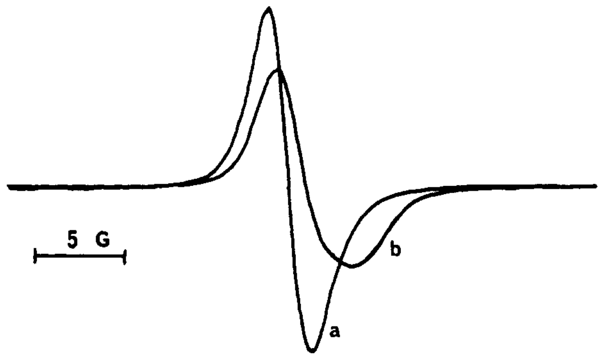

Figure 2. ESR spectra of $1^-,2^+$ as a free-standing film at 6 K: (a) x–y plane perpendicular to applied field; (b) x–y plane parallel to applied field.

The visible, near-IR, and IR spectra are in agreement with the proposed structure. In the IR region there is a carbonyl stretching vibration at 1650 cm^{-1}, the expected position for imide anion radicals.[10] There is also an electronic transition at 2500 cm^{-1} due to charge transfer along the stack as expected for a good conductor.[4] Linear dichroism measurements[11] to be reported elsewhere indicated that the average transition dipole of this band is tilted about 30° up from the x–y plane. In the visible spectrum there is a π–π^* band at 437 nm. This wavelength, which is shifted from 480 nm for the monomeric 1^- in DMF, is also consistent with the proposed stack structure.[1]

In conclusion we report that a cationic polymer causes aggregation of anion radicals in solution, and when these preformed stacks electroprecipitate they form an anisotropic film. The film conductivity is electronic and very dependent on the humidity of the atmosphere around it. Because of the orientation of the stacks, the conductivity is much higher in the plane than in the z direction. It appears that the film could be used as a humidity sensor.

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Registry No. $1^-\cdot2^+$, 135366-30-2.

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[8] The z-direction conductivity may be low by as much as 100 S cm^{-1} because of the contact resistance at the probe polymer interface. An unusual aspect of the conductivity is revealed in voltage–time transients. When a constant current pulse is applied to the outer electrodes, the voltage across the inner electrodes rises rapidly and then falls to the constant value discussed herein. When the current is returned to zero, the voltage pulses in the other direction before returning to zero.

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Synthesis of the Functionalized Cluster $(CH{=}CH_2C_5H_4)Cp_3Fe_4(CO)_4$ and Its Incorporation into Poly(methyl methacrylate)

Mark A. Massa and Thomas B. Rauchfuss*

Beckman Institute and the
School of Chemical Sciences
University of Illinois, Urbana, Illinois 61801

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Transition-metal clusters have found wide usage in the areas of heterogeneous catalysis[1] and more recently as thermally labile precursors to inorganic solids.[2] The structural integrity of the cluster core, however, is usually sacrificed in these applications.[3] An alternative approach

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