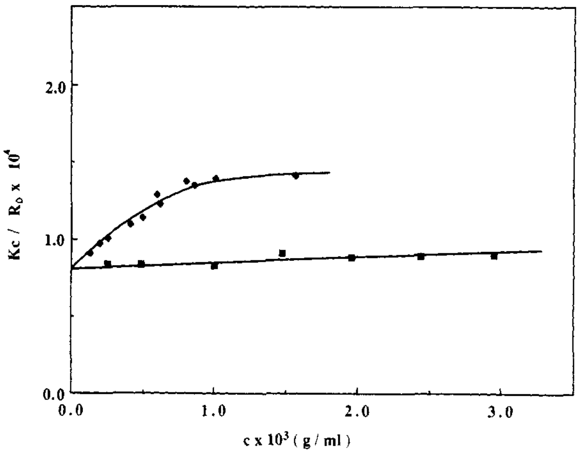

Figure 2. Reciprocal reduced scattered intensity at zero angle, Kc/R_0, against polymer concentration for halato-telechelic ionomer (◆) in DMF as well as for unquaternized polymer (■).

ionomers in polar solvents or in polyelectrolytes in water.

Hara et al.[5] showed that random ionomers (i.e., lightly sulfonated polystyrene) with a very small number of ionic groups (e.g., less than one ionic group per chain on average) showed polyelectrolyte behavior. It was suggested from these observations that the necessary condition to cause polyelectrolyte behavior is the existence of ionic groups in polymer chains, whatever their number is, and that the intermolecular interactions play a major role in polyelectrolyte behavior. The present results on halato-telechelic ionomers seem to confirm the previous conclusions. Since only two ends of the polymer chain have ionic groups that are separated by more than 100 repeating units, it is difficult to apply the conventional explanation of polyelectrolyte behavior; i.e., the intramolecular repulsion between fixed ions on the same chain causes the expansion of the chain, leading to polyelectrolyte behavior.

In addition, as is shown in the value of the functionality (1.85), many chains have only one ionic end group. This fact reinforces our conclusion that the effects observed are intermolecular in nature.

Several models based on intermolecular interactions may be considered to explain the results: Wolff[15] stated that chains were entangled and decreased in size with concentration in the concentration range where the Fuoss equation was applicable. Similar arguments, based on homogeneously entangled semidilute polyelectrolyte solutions, are given by using a scaling approach,[16,17] although this considers a locally rodlike conformation arising from intramolecular repulsion in a very dilute polyelectrolyte solution. Hara and Nakajima[18] suggested the existence of "lamps" which are formed due to inhomogeneous entanglements of polymer chains under repulsive interactions. Ise et al.[19] proposed the formation of a second phase made of macroions, caused by the net attraction of charges having the same sign, via counterions with opposite sign. Whether the interaction is attractive or repulsive, our data strongly suggest the importance of intermolecular interactions in the solution behavior of salt-free polyelectrolytes. More detailed experiments on halato-telechelic ionomers are under way to find the best model to explain the observed behavior.

In summary, typical polyelectrolyte behavior was observed for halato-telechelic ionomers that had ionic groups only at chain ends. Both viscosity and low-angle light scattering experiments showed similar results as those obtained for random ionomers. Although some solution properties of halato-telechelic ionomers have been reported,[20-22] this is the first time that polyelectrolyte behavior is reported for this type of ionomer. It is suggested that the essential factor causing polyelectrolyte behavior is intermolecular in nature. More detailed experiments on the halato-telechelic ionomers are under way. Analyses on these systems and the proper models to explain the results will be reported.

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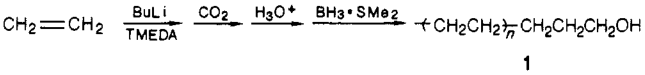
Brønsted Acidity at Polyethylene-Solution Interfaces

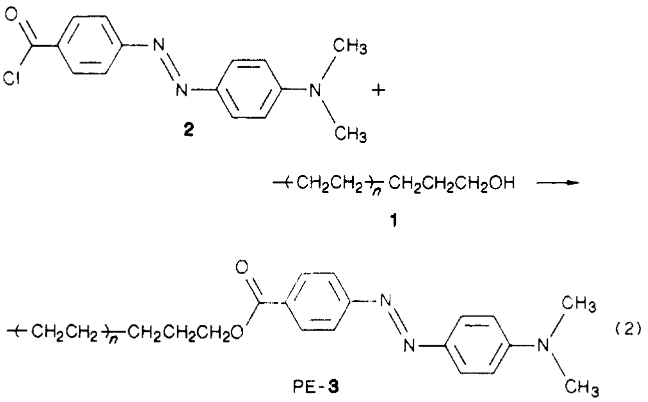
Acid-base chemistry is probably one of the most fundamental aspects of organic chemistry and has received extensive study.[1] It is also widely recognized that acid-base interactions including hydrogen-bonding, proton transfer, and Lewis donor–acceptor interactions are important in polymer chemistry.[2,3] Similarly, acid–base chemistry is an important aspect of the chemistry of functionalized polymers.[4] For example, acid–base chemistry is especially important in technologically important processes like adhesion, adsorption, and polymer blending. In this paper we describe our initial results on studies of acid–base chemistry at polyethylene–solution interfaces using a pH-sensitive azo dye. Our results show that such a dye is a somewhat poorer base when bound to polyethylene. This result is in accord with an earlier report on *decreased* acidity of CO_2H groups at polyethylene–water interfaces.[5,6]

Derivatization of polyethylene to incorporate an appropriate azo dye was accomplished by the procedure we have called entrapment functionalization.[7,8] In this procedure, we first prepared a polyethylene oligomer with a terminal hydroxyl group to which the azo dye was attached (eq 1 and 2). Dissolution of this oligomer with a 10-



$$CH_2{=}CH_2 \xrightarrow[\text{TMEDA}]{\text{BuLi}} \xrightarrow{CO_2} \xrightarrow{H_3O^+} \xrightarrow{BH_3\cdot SMe_2} -\!\!(CH_2CH_2)_n\!\!-CH_2CH_2CH_2OH \quad (1)$$

1



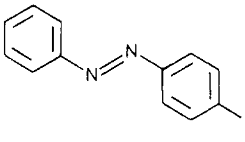
(2)

100-fold excess of additive-free polyethylene in toluene at 100 °C followed by cooling led to formation of polyethylene powder which contained this oligomer and its covalently bound azo dye.[9] Solvent casting of films from dichlorobenzene solutions of oligomer and host polymer at 130 °C was also successful.

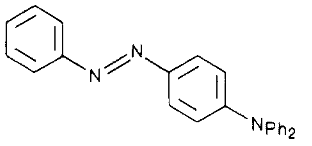
Films or powders containing PE-**3** were light yellow and changed to red on addition of a CH_2Cl_2 solution of CH_3SO_3H or $CH_3(CH_2)_{15}SO_3H$. Methylene chloride suspensions of PE-**3** had λ_{max} at 428 nm while PE-**3**-$H^+CH_3SO_3^-$ had a λ_{max} at 500 nm. The position of λ_{max} for the protonated azo dye varied slightly with changes in solvent (497 nm in toluene, 503 nm in ethyl acetate). Little change was seen in λ_{max} for the neutral starting material in different solvents. These values of λ_{max} were similar to those of the neutral and acid forms of the octyl ester of para-methyl red, C_8H_{17}-**3** and C_8H_{17}-**3**-$H^+CH_3SO_3^-$ (435 and 520 nm, respectively). The differences were in accord with the polyethylene-entrapped dye being in a less polar environment. Other features of PE-**3**-$H^+CH_3SO_3^-$ were more striking. In particular, the facile bleaching of films of PE-**3**-$H^+CH_3SO_3^-$ in contact with water and other oxygenated solvents was unexpected.

The acidity of PE-**3**-$H^+CH_3SO_3^-$ was visibly apparent when samples of PE-**3**-$H^+CH_3SO_3^-$ prepared from PE-**3** and CH_3SO_3H in CH_2Cl_2 were dried and exposed to a humid atmosphere. The red color of the conjugate acid substantially faded. When samples of PE-**3**-$H^+CH_3SO_3^-$ were suspended in solvents like ethanol or tetrahydrofuran faster decolorization occurred. Removal of the water or ethanol in a vacuum reversed this color change. This discolorization of the red PE-**3**-H^+, which was due to formation of neutral PE-**3** from PE-**3**-H^+ (UV–visible spectroscopy), is the result of the acidity of PE-**3**-$H^+CH_3SO_3^-$ and the large excess of the solvent present, which would favor formation of protonated solvent even if PE-**3**-$H^+CH_3SO_3^-$ were less acidic than the protonated solvent. Moreover, this solvent leveling effect with polyethylene-incompatible solvents is significant in that it demonstrates that most of the entrapped PE-**3**-$H^+CH_3SO_3^-$ is located at the polyethylene–solution interface and is accessible to solvent. The interface or phase boundary between a functionalized polyethylene and solution is a poorly defined interface whose dimensions or depth depends on both the exptl. probes used to examine it and on the interaction of the solution with the functionalized interface.[5,7,8] In the case of these studies in organic solvents, the polyethylene–CH_2Cl_2 interface is likely to be deeper than a polyethylene–ethanol or a polyethylene–water interface.[5] Here we consider the interface of polyethylene in contact with solvents to be that region in which entrapped groups can readily chemically interact with polyethylene-insoluble species.

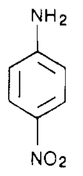
We obtained estimates of the acidity of PE-**3**-$H^+CH_3SO_3^-$ and a comparison to C_8H_{17}-**3**-$H^+CH_3SO_3^-$ in methylene chloride suspensions in several ways. For example, using the Hammett indicators **4**–**8** in CH_2Cl_2,[10] we found that PE-**3**-$H^+CH_3SO_3^-$ quantitatively protonated **4** and **5** partially protonated **6**. The dyes **7** and **8** were, however, not protonated to any measurable extent in CH_2Cl_2. While the H_0 values for these dyes are meaningless in CH_2Cl_2, it appears that PE-**3** is about 1–2 orders of magnitude less basic than **4** or **5** and comparable to **6**.[11] These experiments also showed that PE-**3**-H^+ was qualitatively more acidic than C_8H_{17}-**3**-$H^+CH_3SO_3^-$ since C_8H_{17}-**3**-$H^+CH_3SO_3^-$ did not protonate these same indictors.



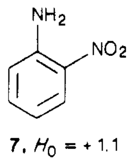
4, H_0 = +2.8



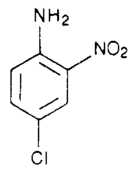
5, H_0 = +1.5



6, H_0 = + 1.1



7, H_0 = + 1.1



8, H_0 = + 1.1

Quantitative data about the acidity of PE-**3**-$H^+CH_3SO_3^-$ versus C_8H_{17}-**3**-$H^+CH_3SO_3^-$ were obtained by using mixtures of PE-**3**-$H^+CH_3SO_3^-$, PE-**3**, C_8H_{17}-**3**-$H^+CH_3SO_3^-$, and C_8H_{17}-**3** in CH_2Cl_2. In these experiments, starting mixtures of PE-**3**-$H^+CH_3SO_3^-$/C_8H_{17}-**3** in molar ratios of 1:5–3:2 and starting mixtures of PE-**3**/C_8H_{17}-**3**-$H^+CH_3SO_3^-$ of 1:1–10:1 were equilibrated and the apparent K_{eq} values for eq 3 were

$$\text{PE-}\mathbf{3} + C_8H_{17}\text{-}\mathbf{3}\text{-}H^+CH_3SO_3^- \rightleftharpoons \text{PE-}\mathbf{3}\text{-}H^+CH_3SO_3^- + C_8H_{17}\text{-}\mathbf{3} \quad (3)$$

calculted by using the ϵ values measured for C_8H_{17}-**3**-$H^+CH_3SO_3^-$ and C_8H_{17}-**3** and the absorbance at equilibrium for C_8H_{17}-**3**-$H^+CH_3SO_3^-$ and C_8H_{17}-**3** in solution and for PE-**3**-H^+ and PE-**3** in the films. These K_{eq} values were measured by starting with an excess of either the soluble or polymer-bound dye as noted in Table I. The apparent

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Table I
Equilibria between PE-3, PE-3-$H^+CH_3SO_3^-$, C_8H_{17}-3, and C_8H_{17}-3-$H^+CH_3SO_3^-$ in CH_2Cl_2[a]

$[\text{PE-3}]_0$/ $[C_8H_{17}\text{-3-}H^+CH_3SO_3^-]_0$	$[\text{PE-3-}H^+CH_3SO_3^-]_0$/ $[C_8H_{17}\text{-3}]_0$	$[K_{eq}]^{-1}$
1/1		4.0
2/1		3.6
10/1		10
	1/5	22
	1/1	3.6
	3/2	5.0

[a] Equilibria were measured at 25 °C in CH_2Cl_2 suspensions. Concentrations were determined after the suspensions were allowed to equilibrate until repetitive scans showed no further changes were occurring in the UV–visible spectrum. The values of ϵ for C_8H_{17}-3 and for C_8H_{17}-3-H^+ were 25 700 and 3990 L/(mol cm) at 435 nm and 2650 and 55000 L/(mol cm) at 520 nm, respectively.

values listed reflect the differing protonating ability of soluble **3** and polymer-bound **3** (i.e., $[K_{eq}]^{-1} = K_{a\,\text{PE-3-}H^+CH_3SO_3^-}/K_{a\,C_8H_{17}\text{-3-}H^+CH_3SO_3^-}$) and ranged from 3.6 to 22. The results in Table I show that the acidity of PE-3-$H^+CH_3SO_3^-$ was greater than that of C_8H_{17}-3-H^+-$CH_3SO_3^-$.

Determinations of the K_{eq} in Table I include several assumptions and are subject to some experimental limitations.[12] For example, attempts to measure equilibrium constants with a large excess of PE-3-$H^+CH_3SO_3^-$ or PE-3 relative to the soluble analogue were frustrated by the small amount of **3** in the polymer sample (typically 10^{-8} mol). Second, use of a large excess of soluble C_8H_{17}-3-$H^+CH_3SO_3^-$ or C_8H_{17}-3 relative to PE-3 or PE-3-H^+-$CH_3SO_3^-$ never produced a true equilibrium because diffusional limitations affected the access of the soluble azo dye to the polymer-bound analogue. Third, we assumed in these calculations of K_{eq} that the ϵ measured for the octyl ester in solution was valid in the polymer matrix and that the concentrations determined in a conventional way from the measured absorbance could be used to calculate a K_{eq} in CH_2Cl_2 suspension. Nonetheless, the data taken together clearly indicate that a protonated polyethylene-bound cationic azo dye is a stronger acid than its souble analogue. These changes in acidity presumably reflect the lower stability of ionic structures within polyethylene. We think such an effect should be a general phenomena for polyethylene-bound cationic acids. Such effects along with the kinetic effects of acid or base size and solvent polarity are important parameters which can govern proton transfers and related chemistry at polyethylene–solution interfaces.

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(9) The polyethylene used in these experiments was high-density polyethylene (M_w 180 000–200 000) and was obtained from Allied Chemical Corp. The powders prepared by these precipitation techniques appeared to exist as small platelets by light microscopy (dimensions of ca. 1 × 1 × 0.02 mm) and were uniformly colored with dye. The cast films were typically 0.5-mil thick.

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Direct Measurement of the Interaction between Mica Surfaces with Adsorbed Diblock Copolymer in a Good Solvent

The use of flexible polymers to stabilize colloidal dispersions is well established.[1] In choosing appropriate stabilizers a number of requirements must be met: the polymer should adsorb strongly, it should extend sufficiently far from the surface (to prevent particles from aggregating due to van der Waals attractions), and the polymer should be in good solvent conditions, to ensure repulsion between the segments in the absorbed layers. In recent years the important role of *bridging* has become apparent: even if the above conditions are observed, for undersaturated surface concentrations polymer chains may readily bridge the gap between the opposing surfaces, adsorbing quasi-irreversibly on both and leading to a net attraction.[2,3] This has been empirically overcome by using diblock copolymers where one block adsorbs while the other extends into the solution or polymers which are end-grafted onto the surface, where one end adsorbs while the rest of the polymer extends into the solution (under good solvent conditions). Recently, force measurements between mica sheets in a polystyrene–poly(2-vinylpyridine) (PS–PVP) diblock copolymer solution have been interpreted in these terms,[4] while very recently forces were measured between mica sheets bearing *end-grafted* polystyrene in toluene[5] (a good solvent for PS). The results of the two studies were rather different both in the range and in the relaxation properties of the forces reported. In this paper we report the measurement of forces between two mica surfaces in a solution of a diblock polystyrene–poly(ethylene oxide) (PS–PEO) copolymer in a good solvent and compare our results critically with the earlier studies.

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