ELSEVIER

Journal of Photochemistry and Photobiology A: Chemistry 126 (1999) 71–76

Journal of Photochemistry and Photobiology A:Chemistry

www.elsevier.nl/locate/jphotochem

Fluorescence spectroscopic probing of two distinctive microenvironments in perfluorinated ionomer membranes

Christopher E. Bunker, Harry W. Rollins, Bin Ma, Kenya J. Simmons, Jin-Tao Liu, Jing-Ji Ma, Charles W. Martin, Darryl D. DesMarteau, Ya-Ping Sun *

Department of Chemistry, Howard L. Hunter Chemistry Laboratory, Clemson University, Clemson, SC 29634-1905, USA

Received 2 September 1998; received in revised form 11 May 1999; accepted 18 May 1999

Abstract

Ethidium bromide was used as fluorescent molecular probe in the understanding of structural properties of Nafion, Dow Chemical, and sulfonimide ionomer membranes. The fluorescence lifetime results show that the probe is located in the interfacial region of the membrane structure, and that the interfacial region is inhomogeneous, consisting of two distinct subsections of different hydrophilicities. The ionomer membranes under consideration have similar structural properties with respect to the ethidium cation probing, despite the fact that their corresponding ionomers have different molecular structures. The fluorescence lifetime results also show that there are considerable mobilities throughout the interfacial region, which allow diffusional quenching processes. Finally, results of effects of hydrothermally stressing Nafion membrane at elevated temperatures on structural properties of the membrane are discussed.

Keywords: Ethidium bromide; Perfluorinated ionomer membranes; Flourescence probing

1. Introduction

Because of their high thermal, mechanical, and chemical stabilities and their excellent ion transport properties, perfluorinated ionomer membranes have recently received much attention for applications in modern battery and fuel cell technologies [1–4]. Current knowledge on structural properties of the membranes is largely from studies of Nafion, a commercial perfluorinated ionomer membrane. It has been proposed that the properties of Nafion membrane may be understood by assuming the presence of reverse micelle-like ion clusters in the membrane structure [5]. According to the model, the ion cluster consists of a hydrophilic water core that is supported by the hydrophobic perfluorinated polymer backbone through an interfacial layer. The water cores in neighboring ion clusters are presumably interconnected through channels, thus facilitating ion transportation through the membrane [5]. The ion cluster model is supported by results from small-angle X-ray scattering measurements [6] and from the experiment in which the hydrophilic cavities in Nafion membrane were used as hosts for preparing metal sulfide nanoparticles [7]. Recently, however, the experimental results in support of the ion cluster model were reevaluated and modifications to the model were suggested [8].

Luminescence spectroscopic methods have been employed to study the structural properties of ionomer membranes and to evaluate the ion cluster model [9–19]. According to results from the quenching of $Ru(bpy)_3^{2+}$ fluorescence by various cations in Nafion membrane, Lee and Meisel suggested that the probe $Ru(bpy)_3^{2+}$ is likely located in the interfacial region of the membrane structure [9]. Further evidence for the presence of a substantial interfacial region in perfluorinated ionomer membranes was obtained in a recent study of a series of environment sensitive fluorescent probes [19]. It was proposed that the interfacial region may be viewed as a heterogeneous mixture of perfluorinated polymer branches and water molecules, where the microscopic environment experienced by the fluorescent molecular probes is effectively close to those in polar organic solvents [19]. Results from luminescence probing experiments have also provided valuable information on transport related processes in perfluorinated ionomer membranes. Lee and Meisel demonstrated that the quenching of $Ru(bpy)_3^{2+}$ fluorescence by various cations in Nafion membrane is dynamic and occurs at a rate similar to that

* Corresponding author.
E-mail address: syaping@clemson.edu (Y.-P. Sun)

1010-6030/99/$ – see front matter
PII: S1010-6030(99)00120-3

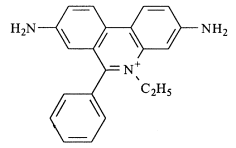
in bulk water [9]. Yeager and Steck also used fluorescence spectroscopy to study ionic diffusion in Nafion membrane, and the results prompted their proposal for a three-region structural model on ion clusters in perfluorinated ionomer membranes [20]. In terms of the three-region model, the ion clusters are amorphous, formed by fluorocarbon backbone materials surrounding a region with high contents of water and sulfonate exchange sites. The interfacial region consists of a mixture of pendent side chains, small amounts of water, non-clustered sulfonate exchange sites, and counterions [20]. The three-region model is in general agreement with what Falk suggested earlier on the basis of a careful infrared absorption study of H_2O and HDO in Nafion membrane [21]. In addition, results from a recent fluorescence study of pyrene excimer formation in Nafion membrane also suggest that there is considerable mobility in the interfacial region of the membrane structure [19]. However, structural details of the interfacial region remain to be better understood. Here, we report a fluorescence spectroscopic probing of perfluorinated ionomer membrane structures using ethidium bromide (**I**) as a probe. The results suggest the presence of two distinct subsections in the interfacial region of the membrane structure.

Ethidium bromide has been widely used in the study of DNA–drug interactions [22]. In an aqueous buffer solution, the ethidium cation is only weakly fluorescent, with a short fluorescence lifetime [23]. However, in the presence of DNA, ethidium cation forms a loosely defined complex with DNA due to the intercalation of the planar cationic ethidium species into the helical structure of DNA [24,25]. The intercalation results in dramatic increases in the fluorescence quantum yield and lifetime of the ethidium cation due to the hydrophobic environment in the DNA structure [23–25]. Thus, the ethidium cation is an ideal probe for studying hydrophilic and hydrophobic environments in perfluorinated ionomer membranes. In our study, microstructures of Nafion (**II**), Dow Chemical (**III**), and sulfonimide (**IV**) ionomer membranes were probed comparatively. The sulfonimide ionomer membrane is being developed as an alternative to Nafion membrane for potentially better structural properties and the ability to be used under more extreme conditions in battery and fuel cell applications [2]. In addition, effects of hydrothermally stressing Nafion membrane at elevated temperatures on structural properties of the membrane were evaluated.

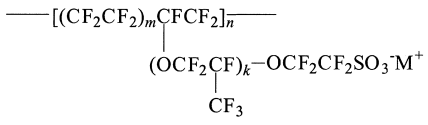
2. Experimental

2.1. Materials

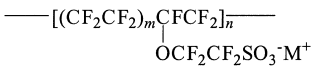
Ethidium bromide (95%) was purchased from Sigma Chemical and used as received. Water was deionized and purified by being passed through a Labconco WaterPros water purification system. Spectroscopy grade organic solvents were used as received. Nafion ionomer (**II**) membrane, with an equivalent weight of 1100, was provided by Du Pont Co. Dow Chemical ionomer (**III**) membrane with, an equivalent weight of 1000, was obtained from Dow Chemical Co. The sulfonimide ionomer (**IV**) was prepared in-house by copolymerizing tetrafluoroethane with the sulfonimide monomer [26,27]. Details on the synthesis will be reported separately. The membrane was obtained by wet casting from a solution of the sulfonimide ionomer (**IV**) in dimethylformimide, followed by careful annealing at a high temperature. The equivalent weight of the sulfonimide ionomer membrane was estimated to be ∼1200 in terms of titration.



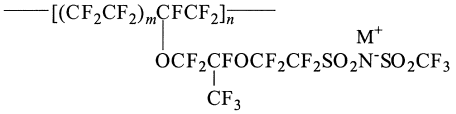
I



II



III



IV

2.2. Sample preparations

The ionomer membranes **II**–**IV** were purified using a uniform treatment procedure to remove colored impurities in the membranes. In the purification, the membranes were immersed in concentrated nitric acid while stirring at 60°C for 24 h. The acid was then decanted and the membranes were placed sequentially in aqueous solutions of 60, 40, and 20% nitric acid, each for 1 h with stirring, followed by washing thoroughly with clean water. The treated ionomer membranes are clear and optically transparent down to 200 nm. Converting the membranes to the sodium form was achieved by soaking the treated membranes in a 0.1M aqueous solution of sodium hydroxide with stirring for 24 h, followed by washing thoroughly with clean water until neutral. The membranes in the sodium form are again clear and optically transparent down to 200 nm. Unless specified otherwise, the membranes used in our fluorescence spectroscopic probing experiments are in the sodium form.

For hydrothermal stressing, a piece of Nafion membrane was placed in a sealed stainless steel vessel filled with pure water. The sealed vessel was thermostated at a given temper-

ature in a tube furnace. After the hydrothermal stressing for 1 h, the Nafion membrane was cooled to room temperature and washed with pure water.

2.3. Measurements

Absorption spectra were measured on a computer-controlled Shimadzu UV-2101PC spectrophotometer. A mask that has a 5 mm diameter hole in the center was used in absorption measurements of the ionomer membranes to insure that all of the transmitted light passes through the sample. Steady-state fluorescence spectra were recorded on a Spex Fluorolog-2 photon-counting emission spectrometer equipped with a 450 W xenon source and an R928 photomultiplier tube (PMT). Fluorescence measurements were made in a right-angle geometry using a home-built sample stage. The film sample was held between two quartz plates that face toward both the excitation light and the detector at a 45° angle. Fluorescence was detected from the back side (the side not facing the excitation beam) of the film sample to minimize the effects of surface scattering.

Fluorescence decays were obtained using the time-correlated single photon counting (TCSPC) method. The TCSPC setup includes a nitrogen flash lamp (Edinburgh Instruments) operated at 50 kHz. The excitation wavelength of 337 nm was isolated using a band-pass filter (10 nm FWHM). Fluorescence decays were monitored through a 380 nm color glass sharp-cut filter. The detector consists of a Philips XP2020 photomultiplier tube (PMT) in a thermoelectrically cooled housing (Products for Research, Co.). The PMT was operated at −2 kV by using an EG&G 556 high-voltage power supply. The detector electronics from EG&G Ortec include two 9307 discriminators, a 457 biased time-to-amplitude converter, and a 916A multichannel analyzer. The instrument response function of the TCSPC setup has a FWHM of ∼2 ns.

3. Results and discussion

Ethidium bromide is soluble in water. The loading of ethidium bromide as a fluorescent probe into the perfluorinated ionomer membranes was accomplished by sonicating the membranes in an aqueous solution of the probe for ∼2 min. Absorption spectra of the ethidium cation in Nafion, Dow Chemical, and sulfonimide ionomer membranes are compared in Fig. 1 with the spectra in aqueous solutions with and without calf thymus DNA. While the spectra in the three membranes are quite similar, they are shifted from the spectra in aqueous solutions: red-shifted from the spectrum without DNA and blue-shifted from the spectrum with DNA (Fig. 1).

Fluorescence spectra of the ethidium cation in Nafion, Dow Chemical, and sulfonimide ionomer membranes are shown in Fig. 1. The spectra are rather similar in the three different kinds of membranes, but blue-shifted from the spectrum in bulk water and slightly red-shifted from the spectrum in an aqueous buffer solution with calf thymus DNA (Fig. 1). Although a quantitative determination of fluorescence quantum yields of the ethidium cation in the ionomer membranes was not successful due to experimental difficulties associated with thin film measurements, observed fluorescence intensities of the ethidium cation in the ionomer membranes are much higher than those in bulk water. Since water quenches the ethidium cation excited state, the fluorescence of the ethidium cation is higher in a more hydrophobic environment. Thus, with the higher observed fluorescence intensities of ethidium bromide in ionomer membranes, it seems likely that the probe species are located in the interfacial region of the membrane structure.

Table 1
Fluorescence lifetimes of ethidium bromide in perfluorinated ionomer membranes

Medium	$\tau_{F,1}$ (ns)	$\tau_{F,2}$ (ns)	a_1/a_2[a]
Nafion membrane	3.2	12	0.8
Dow Chemical membrane	2.6	13	0.4
Sulfonimide membrane	3.0	14	0.65
Water	1.7	–	–
Aqueous solution with DNA	22	–	–

[a] a_1 and a_2 are the pre-exponential factors in bi-exponential decay equation.

Fluorescence decays of the ethidium cation were measured using the TCSPC technique. For the ethidium cation in bulk water, the observed fluorescence decay can be deconvoluted from the instrument response function using a single exponential decay equation. The fluorescence lifetime thus obtained is 1.7 ns, in excellent agreement with the literature results [23]. In an aqueous buffer solution in the presence of calf thymus DNA, the fluorescence of the ethidium cation is much longer-lived, and the decay is still single exponential. The fluorescence lifetime of 22 ns thus obtained also agrees well with the results reported in the literature [23]. However, fluorescence decays of the ethidium cation in the perfluorinated ionomer membranes are considerably different. In Nafion membrane, the observed fluorescence decay of the ethidium cation can only be deconvoluted from the instrument response function using a bi-exponential decay equation (Fig. 2). The lifetimes of the two fluorescence components are 3.2 ns and 12 ns, which are both longer than the fluorescence lifetime of the ethidium cation in bulk water, but shorter than that in the aqueous buffer solution with DNA (Table 1). Similar fluorescence decays were obtained for ethidium bromide in Dow Chemical and sulfonimide membranes (Fig. 2). The decays are both bi-exponential, and the two lifetimes obtained from each decay curve are similar to those for ethidium bromide in Nafion membrane (Table 1).

The two components in observed fluorescence decays may be attributed to the probe molecules located in two distinctively different environments in the interfacial region of the ionomer membrane structure. The assignment that the probe ethidium cation species are located in the interfacial region is justified because both fluorescence components have life-

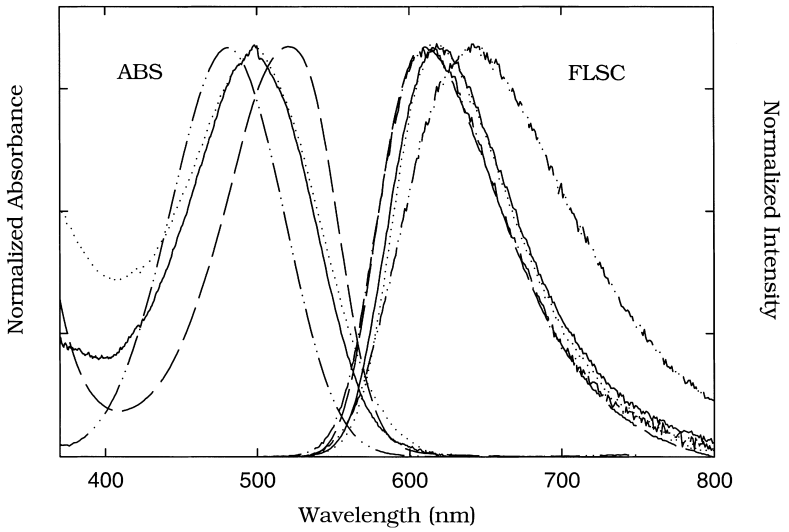


Fig. 1. Absorption and fluorescence spectra of ethidium bromide in Nafion membrane (———), Dow Chemical membrane (·····), and the sulfonimide ionomer membrane (-·-) are compared with the spectra in water (-···-) and in an aqueous buffer solution with calf thymus DNA (— — —).

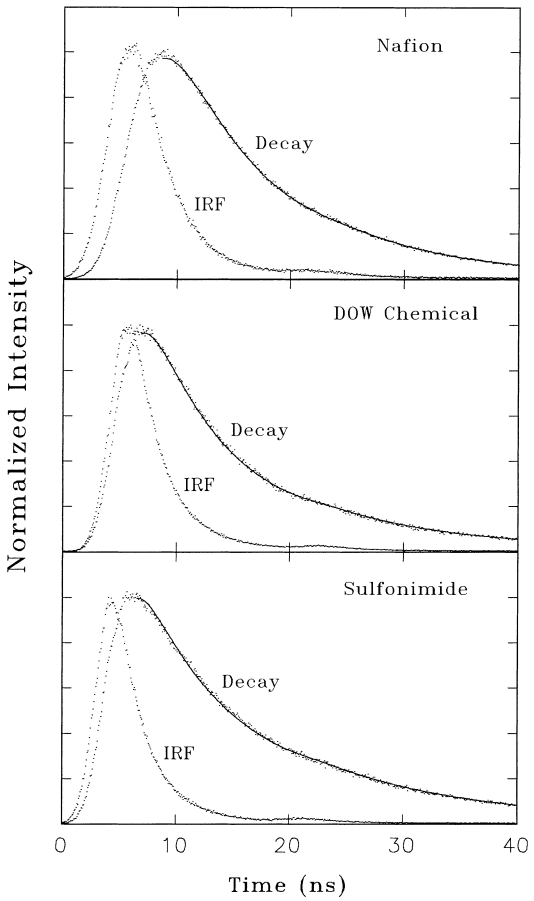


Fig. 2. Fluorescence decays of ethidium bromide in perfluorinated ionomer membranes.

times longer than that for the ethidium cation in bulk water. The fluorescence lifetime results also suggest that the interfacial region of the ionomer structure must be substantial and inhomogeneous, with subsections of different degrees of hydrophilicity (or hydrophobicity). The presence of a substantial interfacial region in the ionomer membrane structure is also supported by other experimental results [8,9,19–21]. According to the extended ion cluster model for structural properties of perfluorinated ionomer membranes [19,20], the interfacial region may be viewed as a heterogeneous mixture of perfluorinated polymer branches and water molecules. Thus, the subsection next to the polymer backbone is likely more hydrophobic due to a higher content of polymer branches, whereas the subsection close to the water core is likely more hydrophilic due to more water molecules in the heterogeneous mixture. However, it is interesting that the probe ethidium cation species are localized predominantly in two distinctively different subsections instead of in a distribution of gradually varying environments. The localization of probe species in only two different environments could be a reflection of some structural constraints that are not explained in the current ion cluster model for perfluorinated ionomer membranes. It may also be associated with the properties of the probe. The ethidium cation consists of both hydrophobic and hydrophilic groups and is soluble in both organic and aqueous media. Because of such properties, the ethidium cation species probably prefer microscopic environments that are either highly hydrophobic or more hydrophilic.

The ethidium cation excited state is quenched by organic anionic species [23]. For the ethidium cation in Nafion membrane, the quenching of fluorescence lifetime by acetate anion was investigated. In the sample preparation, a piece of Nafion membrane pre-loaded with the ethidium cation was soaked in a sodium acetate solution (1.3×10^{-2} M) for ~1 h. The piece of membrane was then washed with pure water to remove any ethidium cation or acetate anion species on the membrane surface. The ethidium cation fluorescence decay in the Nafion membrane loaded with acetate anion

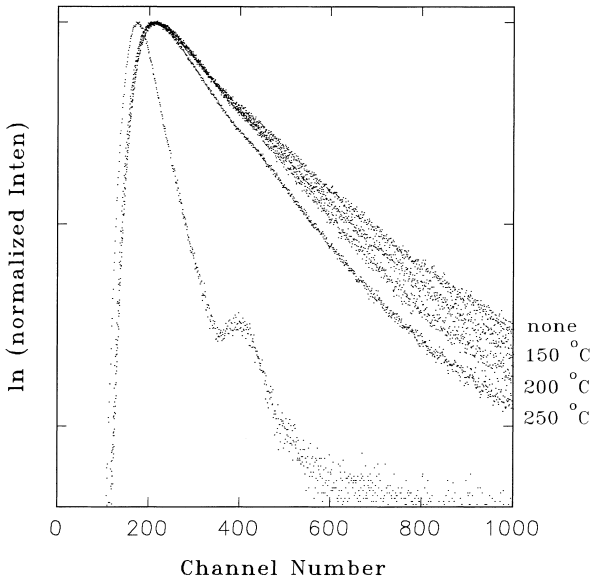


Fig. 3. Fluorescence decays of ethidium bromide in as-prepared and hydrothermally-stressed Nafion membranes. The decay curves are marked with the stressing temperatures.

remains bi-exponential, but the overall decay is faster than that in the absence of the anionic quencher. The lifetimes of the two fluorescence components are 1.6 and 9.7 ns, respectively, both shorter than those in the membrane without acetate anion. The results indicate that the ethidium cation species in the hydrophobic and more hydrophilic subsections of the interfacial region in the Nafion membrane structure are subject to fluorescence quenching effects and that the quenchings are dynamic in nature. It implies that diffusional processes occur not only in the interfacial region of the ionomer membrane structure, but also occur throughout the region. However, the quenching is apparently more significant in the more hydrophilic subsection, corresponding to a much higher fluorescence lifetime quenching ratio. The different quenching efficiencies might be a result of the distribution of the quencher acetate anion species in the two subsections.

An important application of perfluorinated ionomer membranes is in batteries and fuel cells. In such uses, ionomer membranes are typically subject to harsh operational conditions [2–4]. Among issues to be understood is the effect of hydrothermal stressing of ionomer membranes on their structural properties. For a systematic examination, a series of Nafion membrane pieces that were hydrothermally stressed at 150, 200, and 250°C were loaded with the probe ethidium bromide. Fluorescence decays of the ethidium cation in the hydrothermally stressed Nafion membranes were determined. As shown in Fig. 3, the decays remain bi-exponential, but become progressively faster overall in the membrane pieces that were subject to thermal stressing at higher temperatures. Fluorescence lifetimes of the ethidium cation in the Nafion membranes hydrothermally stressed at different temperatures are shown in Table 2. The shorter-lived fluorescence component seems marginally

Table 2
Fluorescence lifetimes of ethidium bromide in hydrothermally stressed Nafion membranes

Stressing temperature (°C)	$\tau_{F,1}$ (ns)	$\tau_{F,2}$ (ns)	a_1/a_2[a]
No stressing	3.2	12	0.8
150	3.3	11	0.9
200	3.2	10.5	0.6
250	3.0	9.3	0.95

[a] a_1 and a_2 are the pre-exponential factors in bi-exponential decay equation.

affected by the hydrothermal stressing, whereas the lifetime of the longer-lived fluorescence component becomes shorter in a membrane hydrothermally stressed at a higher temperature. The results show that the hydrothermal stressing of Nafion membrane has more significant effect on microscopic structures in the more hydrophobic area of the interfacial region. The stressing probably causes some membrane structural damages, so that water molecules are allowed easier access to the more hydrophobic area of the interfacial region. In fact, the hydrothermally stressed Nafion membrane also shows changes in physical properties. The membrane pieces hydrothermally stressed at 150 and 200°C appear stretched, with the overall size larger than that before the hydrothermal stressing, and the piece stressed at 250°C appears damaged such that it is swollen and becomes rubbery and easily torn. The water content also is higher in the membrane hydrothermally stressed at a higher temperature [19].

In summary, ethidium bromide is an excellent fluorescent molecular probe for the understanding of structural properties of perfluorinated ionomer membranes. The fluorescence lifetime results show that the probe is located in the interfacial region of the membrane structure and that the interfacial region is inhomogeneous, consisting of two distinct subsections of different hydrophilicities. Interestingly, the three ionomer membranes under consideration have similar structural properties with respect to the ethidium cation probing, despite the fact that their corresponding ionomers have different molecular structures. Mechanistically, it remains to be understood that the probe ethidium cation species are located predominantly in only two distinctly different subsections, instead of in a distribution of varying environments in the interfacial region of the membrane structure. There are also considerable mobilities throughout the interfacial region, which allow diffusional fluorescence quenching processes. Finally, the hydrothermal stressing of Nafion membrane likely causes membrane structural damages, making the interfacial region overall more hydrophilic. Further spectroscopic studies of the ionomer membrane structures using other hydrophilicity-sensitive molecular probes will be pursued.

Acknowledgements

Financial support from the Department of Energy through DoE/EPSCoR cooperative agreement DE-FG02-91ER75666

is gratefully acknowledged. KJS was a participant in the Summer Undergraduate Research Program, sponsored jointly by the National Science Foundation (CHE-9100387 and CHE-9619573) and Clemson University.

References

[1] S.G. Cutler, in: A. Eisenberg (Ed.), Ions in Polymers, Ch. 9, American Chemical Society, Washington, DC, 1980, Adv. Chem. Ser. No. 187.
[2] A. Eisenberg, H.L. Yeager (Eds.), Perfluorinated Ionomers Membranes, American Chemical Society, Washington, DC, 1982, ACS Symp. Series No. 180.
[3] A.B. La Conti, A.R. Fragala, J.R. Boyack, in: J.D. McIntyre, S. Srinivasan, F.G. Will (Eds.), Electrode Materials and Processes for Energy Conversion and Storage, The Electrochemical Society, Princeton, NJ, 1977, 354 pp.
[4] A.J. Appleby, F.R. Foulkes, Fuel Cell Handbook, Ch. 10, Van Nostrand Reinhold, New York, 1989.
[5] T.D. Gierke, Pres. 152nd National Meeting of the Electrochemical Society, 10–14 October, 1977, Atlanta, GA.
[6] S.C. Yeo, A. Eisenberg, J. Appl. Poly. Sci. 21 (1977) 875.
[7] Y. Wang, A. Suna, J. McHugh, E.F. Hilinski, P.A. Lucas, R.D. Johnson, J. Chem. Phys. 92 (1990) 6927.
[8] A.M. Litt, Polymer, preprint 38 (1997) 80.
[9] P.C. Lee, D.J. Meisel, J. Am. Chem. Soc. 102 (1980) 5477.
[10] I. Nagata, R. Li, E. Banks, Y. Okamoto, Macromolecules 16 (1983) 903.
[11] J.P. Kuczynski, B.H. Milosavljevic, J.K. Thomas, J. Phys. Chem. 88 (1984) 980.
[12] M.N. Szentirmay, N.E. Prieto, C.R. Martin, J. Phys. Chem. 89 (1985) 3017.
[13] E. Blatt, A. Launikonis, A.W.-H. Mau, W.H. Sasse, Aust. J. Chem. 40 (1987) 1.
[14] H. Mohan, R.M. Iyer, J. Chem. Soc., Faraday Trans. 88 (1992) 41.
[15] J.L. Colon, C.R. Martin, Langmuir 9 (1993) 1066.
[16] J.T. Kunjappu, Colloids and Surfaces A 89 (1994) 37.
[17] M.A. Robertson, H.L. Yeager, Macromolecules 29 (1996) 5166.
[18] F.C. Anson, H.B. Gray, E. Sabatani, H.D. Nikol, J. Am. Chem. Soc. 118 (1996) 1158.
[19] C.E. Bunker, B. Ma, K.J. Simmons, H.W. Rollins, J.-T. Liu, J.-J. Ma, C.W. Martin, D.D. DesMarteau, Y.-P. Sun, J. Electroanal. Chem. 459 (1998) 15.
[20] H.L. Yeager, A. Steck, J. Electrochem. Soc. 128 (1981) 1880.
[21] M. Falk, Can. J. Chem. 58 (1980) 1495.
[22] A.R. Peacocke, in: R.M. Acheson (Ed.), Acridines, 2nd ed., Wiley, New York, 1973, p. 723.
[23] J. Olmsted, D.R. Kearns, Biochemistry 16 (1977) 3647.
[24] J.-B. Le Pecq, Methods Biochem. Anal. 20 (1971) 41.
[25] V.W. Burns, Arch. Biochem. Biophys. 133 (1969) 420.
[26] D.D. DesMarteau, J. Fluorine Chem. 72 (1995) 203.
[27] D.D. DesMarteau, US Patent No. 5,463,005.