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Laser fluorimetry studies of ionpair aggregation in ionomers derived from copolymers and polymer containing 2-vinylfluorene

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Summary

Time resolved fluorescence technique was used to demonstrate physically the ionpair aggregation phenomena in the ionomers containing fluorenylsodium as the pendant group along the polymer chains in THF at 25°C. It was found that ionpairs in the ionomer with mole fraction of fluorenylsodium equal to 0.02 did not associate to form stable aggregate. However, the ionpairs would aggregate in those ionomers with higher fluorenylsodium contents. In the homopolymer of vinylfluorenylsodium, extensive aggregation of the ionpairs was observed.

Introduction

Ionomers with ionpairs attached to their hydrocarbon backbones show distinctive properties in dilute organic solutions. It was reported that the viscosities of the nonpolar organic solutions of the lightly sulfonated polystyrene increase with flow rate (1,2). In polar organic solvents, however, these ionomers behave as typical polyelectrolytes (3). In a static light scattering study of the ionomer in THF, it was observed that the second virial coefficient decreases with increasing sulfonate content along the polystyrene backbones (4). To explain these unusual observations, it was suggested that the ionpairs anchored on the polymer chains aggregate to a certain extent which depends on the nature of the solvents, counter ion, and the content of ionpair in the polymer chains.

To provide direct evidence for the aggregation of ionpairs bound to a polymer chain, we employed time resolved fluorescence technique to study a series of ionomers, namely the sodium salts of poly(2-vinylfluorene), copolymers of 2-vinylfluorene-styrene, and the model compounds, 1,3-di(2-fluorenyl)butane and 2-ethylfluorene, in THF at 25°C, whose structures are shown in Figure 1. The reason for choosing these systems is that the uv-visible and fluorescence spectroscopic information and the ionpair structures of fluorenylsodium in THF have been well studied and documented (5,6).

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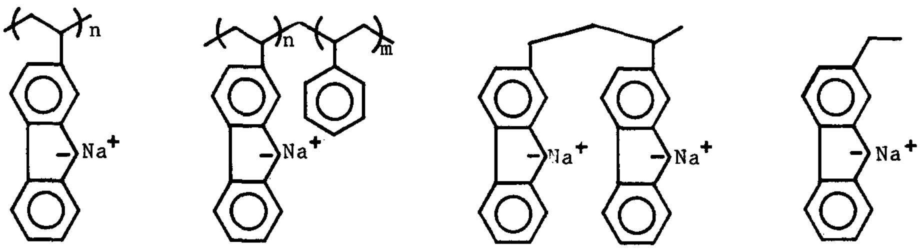


poly(2-vinylfluorenylsodium) [PVFlNa]

Copolymers of 2-vinylfluorenylsodium and styrene [CoPVFlNa-ST]

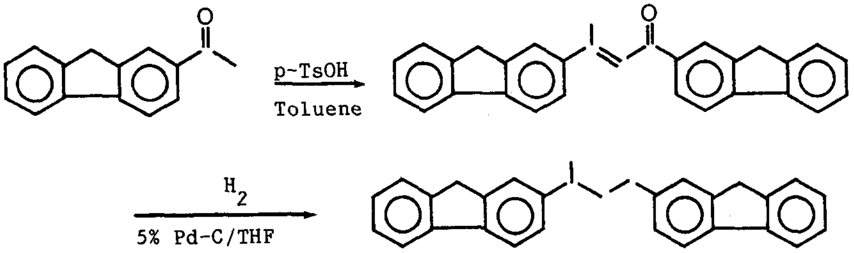
1,3-di(2-fluorenylsodium)butane [DFlNa]

2-ethylfluorenylsodium [EFlNa]

Figure 1. Structures of the sodium salts derived from fluorene containing polymer, copolymer, dimer and monomer.

Experimental

Sample preparation. Poly(2-vinylfluorene) was prepared by the polymerization of 2-vinylfluorene in benzene at 75°C for 50 hours under vacuum using AIBN as initiator (7). The copolymers with different contents of 2-vinylfluorene and styrene were polymerized at different monomer feed ratios under similar conditions as in the homopolymerization except that the extents of reaction were kept at less than 5% conversion. The polymers were purified by repeated precipitation twice in methanol and dried at room temperature by a vacuum oven. The number average molecular weights of the polymers were determined in benzene by vapor pressure osmometer (KNAUER model 1100). The mole fraction of vinylfluorene in the copolymers were determined by measuring the uv absorbance at 306 nm and also from the integration of the NMR spectra of these copolymers. The model compound, 1,3-di(2-fluorenyl)butane which were named as the "dimer" was synthesized according to the following steps:



The dimer, m.p. 163.5-164.5°C, was purified by recrystallization in n-heptane. The monomer, 2-ethylfluorene, m.p. 98-99°C was prepared by hydrogenation of 2-vinylfluorene using 5% palladium on charcoal as the catalyst in ethyl acetate at room temperature and purified by recrystallization in ethanol. The structures of the dimer and monomer were identified by the 250 MHz (Bruker) proton NMR spectra and the high resolution mass spectra (VG70-70F). The conversion of the neutral fluorene groups in the polymers and the model compounds to sodium salts was carried out by reacting with the sodium salt of 1,1,4,4-tetraphenylbutane dianion in THF under high vacuum (10^{-6} torr) and the resulting salt solutions were stored in freezer at about -20°C (7).

Fluorescence Measurement. Steady state fluorescence spectra of the ionpairs were recorded on a Perkin-Elmer model LS-5 luminescence spectrometer. The excitation wavelength was set at 357 nm which, in all cases, was the uv-absorption maximum of the ionpairs in THF and the fluorescence emission was scanned from 400 nm to 800 nm.

The fluorescence decays of the fluorenylsodium ionpair in the homopolymer, copolymers and the model compounds were measured by a pulse laser fluorimeter with the 355 nm output of a Quanta-Ray DCR-2 Nd: YAG laser as the excitation source. A Jarrel-Ash monochromater (Model 82-477) was used to analyze the fluorescence, and the intensity was detected by a Hamamatsu R331 photomultiplier. The phototube signal was sampled by a boxcar integrator (Princeton Applied Research Model 162 with sampling head unit 163) and the analog boxcar output was digitized as a function of time with an 8 bit A/D convertor and stored in a microcomputer system for analysis. Because of the finite duration of the laser excitation pulse (about 6 ns), the measured fluorescence decay profile and the excitation profile must be treated by deconvolution techniques to extract kinetic information. In this study, we used the phase plane method (8) which is suitable for a single exponential decay and the nonlinear least square iterative deconvolution method (9) which is applicable to multi-exponential decays. After the kinetic parameters had been obtained, they were used to generate a decay curve by reconvolution integral and this curve was compared with the experimental decay curve. Statistical methods such as residue plot and autocorrelation functions were used to ensure an acceptable fitting of these curves. All calculation and fitting were done by an IBM 3031B-MVS mainfram system.

Results and Discussion

Four vinylfluorene and styrene copolymer samples with vinylfluorene mole fraction [F_{VFlH}] varying from 0.02 to 0.72 have been prepared by radical machanism at low conversion, which ensured the random distribution of the fluorene moiety along the polymer chain. The reactivity ratios for the VFlH-ST copolymerization system were found to be $R_{VFlH} = 3.51$ and $R_S = 0.58$ according to the method proposed by Kelen and Tudos (10). It is interesting to see that 2-vinylfluorene is much more reactive than styrene in copolymerization.

The spectra of the sodium salts of 2-ethylfluorene, [EFlNa], 1,3-di(2-fluorenyl)butane [DFlNa], poly(2-vinylfluorene) [PVFlNa] and the copolymers with different vinylfluorene contents [CoPVFlNa-ST] at concentration of about 1.0×10^{-4}M in THF all show an absorption maximum at 357 nm which indicates that the salts exist as contact ionpair (5). Steady state fluorescence spectra of the ionpairs in the polymers and the model compounds were obtained by exciting the sample at 357 nm and scanning the fluorescence emission from 400 nm to 800 nm. These spectra which show two peaks centered at 533 nm and 576 nm are similar to that of fluorenylsodium in THF and THP reported by Hogen-Esch and Plodinec (6). It was suggested that the doublet was due to the transitions from the first excited state to two different vibrational levels of the ground state, and not due to two different species such as contact ionpair and solvent separated ionpair or ionpairs in nonaggregated and aggregated forms. It is worthwhile to point out that the bandshapes of the fluorescence emission spectra of the ionpairs remain the same regardless of the variation in the mole fraction of VFlNa in the copolymers. This suggests that the ionpairs do not interact to form excimers, because for aromatic homopolymers and copolymers, excimer formation often leads to a new emission band at a slightly longer wavelength than that of the monomeric emitting species(11).

Ionpair solutions in THF were excited with 355 nm laser output and the fluorescence emission was monitored at 533 nm. The fluorescence decay of EFlNa at concentration of 1.0×10^{-4}M in THF could be fitted by a single exponential decay function:

$$I_{(t)} = A\exp(-\frac{t}{T})$$

It was found that the decay lifetime T was 36.9 ns which is consistent with the reported lifetime of fluorenylsodium in THP (6). Based on the spectrometric study, it was reported that fluorenylsodium, a very similar species with EFlNa, exists mainly as the nonaggregated contact ionpair in THF at 25°C in the concentration range between 10^{-2} M to 10^{-3} M (12). The extent of dissociation, calculated from the dissociation constant of 6.2×10^{-7} M, at a total ionpair concentration of 1.0×10^{-4} M was less than 8% (13). Because of the structural similarity between fluorenylsodium and 2-ethylfluorenylsodium, it is reasonable to conclude that the species responsible for the single exponential decay should be the contact ionpair. The contribution to the total fluorescence emission due to the free ion and the ionpair aggregate, if there is any, is insignificant.

The fluorescence decay profile of the sodium salt of 1,2-di(2-fluorenyl)butane in THF could not be fitted by a single exponential function. Nevertheless, a double exponential decay law in the form of:

$$T_{(t)} = A_1\exp(-\frac{t}{T_1}) + A_2\exp(-\frac{t}{T_2})$$

with T_1 = 30.7 ns and T_2 = 5.2 ns can well describe the fluorescence decay behavior. The double exponential decay of the ionpair in the dimer indicates that there are two fluorescence species in the system. In a conductometric study of intramolecular ionic interactions in bolaform electrolytes of α,ω-bis(9-fluorenyl)polymethylenes in THF, it was revealed that the triple ion formation took place with cesium as the counterion (14), a case similar to the triple ion formation from the free ions in solvents of low dielectric constant (15). However, the extent of this triple ion formation was not significant when sodium was the counterion (14). In our dimeric ionpair, we used sodium as the counterion and, therefore, it is not unreasonable to rule out the triple ion as one of the emitting species. As shown in Figure 2, the dimer can exist in two different structures, namely the extended and the aggregated conformations. The ionpair with the extended structure is expected to have a lifetime similar to that of 2-ethylfluorenylsodium, while the ionpair with

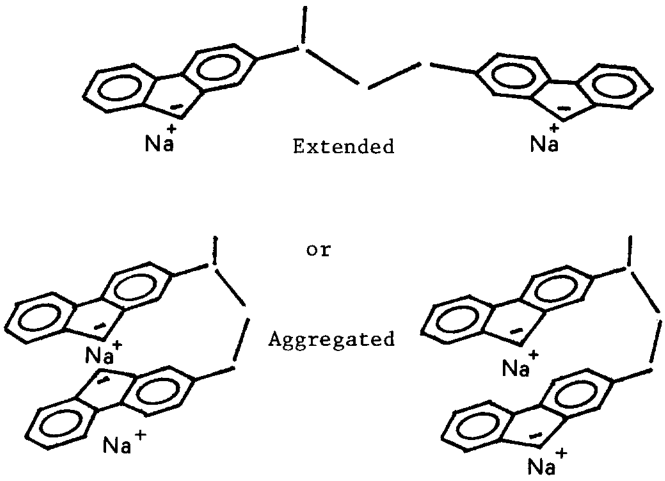


Figure 2. Possible structures of the sodium salt of 1,3-di(2-fluorenyl)-butane

Table 1. Decay Parameters for Fluorenylsodium Anchored on Different Ionomers in THF at 25°C (Ionpair Concentration $\sim 1.0 \times 10^{-4}$M)

Sample	$\bar{M}n$	F_{VFlNa}	A_1	T_1 (ns)	A_2	T_2 (ns)	$\frac{A_2}{A_1+A_2}$	χ^2
CoPVFlNa-ST	35000	0.02	0.126	34.5	-	-	-	3.35
CoPVFlNa-ST	21000	0.07	0.127	23.4	0.085	2.6	0.40	2.40
CoPVFlNa-ST	16000	0.15	0.143	24.7	0.064	3.2	0.31	2.59
CoPVFlNa-ST	13400	0.72	0.086	10.1	0.223	2.9	0.72	2.94
PVFlNa	8500	1.0	0.087	9.4	0.221	3.1	0.72	3.56
DFlNa	-	-	0.113	30.7	0.079	5.2	0.41	2.13
EFlNa	-	-	0.132	36.9	-	-	-	4.12

aggregated structure should have a much shorter lifetime due to the large perturbation leading to a faster rate of dispersion of the excited state energy. Therefore, it is reasonable to assign the species with lifetime of 30.7 ns as the nonaggregated ionpair and the species with lifetime of 5.2 ns as the aggregated ionpair.

The fluorescence decay parameters of the ionpair in different environments, evaluated from the decay curves, are listed in Table 1. The fluorescence decay behavior of CoPVFlNa-ST with $F_{VFlNa} = 0.02$ at ionpair concentration of 1.0×10^{-4} M in THF could be described by a single exponential decay law with a decay lifetime of 34.5 ns, comparable to that of EFlNa. The single exponential decay indicates that there is only one kind of fluorescence species in the excited state which, also based on the uv-visible absorption maximum, is the nonaggregated contact ionpair. This is reasonable since at such low content of fluorenylsodium chromophore along the polymer chain and low overall ionpair concentration it is very difficult for the ionpairs to associate into ionpair aggregates and therefore, each ionpair could be regarded as an isolated fluorescence center.

For the copolymers with mole fraction of VFlNa ranging from 0.07 to 0.72 and poly(vinylfluorenylsodium), the fluorescence decays at ionpair concentration of about 1.0×10^{-4} M in THF could not be fitted by a single exponential function, but could be reasonably well fitted by using a sum of two exponentials, which is similar to the case of the dimer, DFlNa. Double exponential fluorescence decay indicates that there are at least two different kinds of emitting species in the excited state. The species with shorter lifetime is the ionpair aggregate in the copolymers and the homopolymer. The lifetimes lie in the range of 2.9±0.3 ns which does not vary much with respect to the mole fraction of VFlNa in the copolymers. The degree of aggregation inside the copolymers might depend on the distribution of ionpair along the polymer chain. In other words, dimeric, trimeric or higher aggregates could exist along the polymer chain. However, our observation reveals that the shorter lifetime is insensitive to the degree of aggregation. We have also attempted to fit the experimental curve with a triple exponential decay, but the fitting did not show any improvement. This is probably due to either the curve fitting technique cannot differenciate the double exponential decay from the higher exponential decays or all those aggregates have very similar decay lifetime.

The species with longer fluorescence lifetime are the non-aggregated ionpairs. The decay lifetimes of the copolymers with 0.07 and 0.15 mole fraction of vinylfluorenylsodium are approximately the same, which are shorter than that of the monomer, 2-ethylfluorenylsodium. The decrease of the lifetime of the nonaggregated ionpair is probably due to combined factors such as energy transfer to other groups and to the chain that provide ways to dissipate the excited state energy. It is interesting to see that the lifetime of 10.1 ns for the copolymer with 0.72 mole fraction of vinylfluorenylsodium is very close to that for the homopolymer. Together with the similar shorter lifetime (2.9 ns and 3.1 ns) it is suggested that the aggregation phenomena in these two ionomers are very similar to each other.

The extent of aggregation can be related to the relative fluorescence intensities of the short lifetime and long lifetime species. For the copolymers with low vinylfluorenylsodium content, the contribution of the shorter lifetime term to the total fluorescence emission is low [low $A_2/(A_1+A_2)$ value]. However, for the copolymers with high ionpair contents and also the homopolymer, the shorter lifetime term becomes important and contributes more to the total fluorescence decay. This implies that ionpair aggregation takes place most likely in the copolymer with crowded ionpairs along the polymer chain. This ionpair aggregation should be intramolecular because, in these systems, no precipitation was observed during the metallation of the copolymers, whereas intermolecular ionpair aggregation often leads to a decrease in ionomer solubility (7). In the homopolymer the ionpairs are intramolecularly associated into a large aggregate and only the terminal ionpairs have a chance to exist as the nonaggregated species, a case similar to the extended structure of the dimer DFlNa. This extensive ionpair aggregation along the polymer chain has been suggested to explain the decrease of the uv-visible molar absorptivity in poly(vinylfluorenylsodium) in THF and the uv-visible absorption maximum shift of poly(vinylfluorene) in DME from partial metallation to almost complete metallation by the sodium salt of 1,1,4,4-tetraphenylbutane dianion (7). Recently it was also reported that even if the ionpair remained as contact ionpair, a blue shift of the uv-visible absorption maximum was observed when the ionpairs in poly(vinylfluorenylpotassium) aggregated (16).

In conclusion, by using time resoved fluorescence technique, we are able to demostrate physically the existence of two different species, namely the nonaggregated and the aggregated ionpairs in the ionomers. In copolymer with very low ionpair content, the ionpair tends to remain as an isolated species due to the unfavourable loss of entropy in aggregation. However, as the ionpair content in the ionomers increases, the ionpair starts to aggregate and an extensive aggregation of the ionpairs along the polymer chain is achieved in the homopolymer system.

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