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Solvation of Poly(Ion Pairs)Derived from Poly(2-Vinylfluorene)

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Summary

Poly(2-vinylfluorene) was metallated in tetrahydrofuran (THF) and 1,2-dimethoxyethane (DMF) by means of the sodium salt of the dianion dimer of 1,1-diphenylethylene. Initially, the formation of poly(2-vinylfluorenylsodium) is very rapid, but slows down drastically in the later stages of the reaction. Quantitative metallation was accomplished in both solvents. Spectrophotometric evidence in DME as solvent points to a loose fluorenyl ion pair structure at low degrees of metallation, but the structure changes to that of a predominantly tight ion pair when metallation is completed. In THF only tight ion pairs are stable at room temperature, independent of the degree of metallation, but the molar absorptivity of the carbanion has decreased by nearly thirty percent when the polymer is fully metallated.

Introduction

Ionic species tend to associate into ion pairs in low polarity media. Depending on solvent structure, counterion, temperature and other variables, different kinds of ion pairs can exist, for example, externally solvated tight ion pairs and solvated loose ion pairs (SZWARC, 1972 and 1974; SMID, 1972; HOGEN ESCH, 1977). When bound to a polymer chain, either permanently or via polymer-bound ligands, inter- or intramolecular interactions between the ions or ion pairs can drastically affect their dissociation, solvation or reactivity behavior (MORAWETZ, 1975).

While the behavior of polyelectrolytes has been studied extensively in aqueous and other high polarity media, data in ethereal or hydrocarbon type solvents are far less abundant. In earlier investigations we used carbanions of fluorene and substituted fluorenes as sensitive spectrophotometric probes in determining structures of ion pair solvation complexes in low polarity solvents. This led to the discovery of the existence of different kinds of ion pairs in solutions of carbanions and radical anions (HOGEN ESCH and SMID, 1966). Subsequent work on bolaform electrolytes consisting of two terminal fluorenyl carbanions linked by a polymethylene chain of variable length demonstrated the existence of intramolecular ion-ion pair and ion pair-ion pair interactions in these species affecting their solvation and reactivity behavior (COLLINS and SMID, 1973, COLLINS, et al, 1978, TAKAKI, et al, 1978, MATHIS, et al, 1981).

We now report preliminary results on the structures of polymer-bound ion pairs derived from poly(2-vinylfluorene) as a function of the

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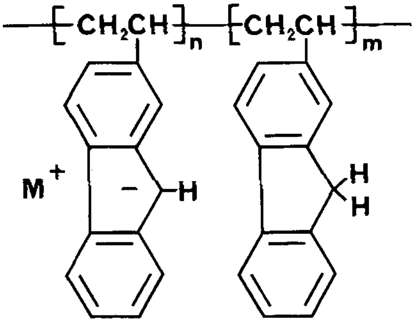
degree of metallation (see structure below). The results show that the



solvation state of the ion pairs can change with the population of carbanions along the chain.

Experimental

Poly(2-vinylfluorene) (PVFl·H) of M_n 23,000 was obtained by polymerization of 2-vinylfluorene in benzene at about 70°C with ABIN as initiator. The monomer (mpt 136-137°C) was synthesized by reduction of 2-acetofluorene (Aldrich) with $NaBH_4$ in ethanol, followed by dehydration of the alcohol in benzene with p-toluenesulfonic acid.

Metallation of the polymer was carried out under vacuum in a glass-enclosed apparatus employing a titration procedure previously used in the determination of molar absorptivities of carbanion salts (AMBROZ et al, 1972). Conversion into poly(2-vinylfluorenyl) ($PVFl^-Na^+$) was accomplished by adding aliquots of the sodium salt of the dianion dimer of 1,1-diphenylethylene, $Na^+,^-C(Ph)_2CH_2CH_2(Ph)_2C^-Na^+$ ($^-DD^-$), using either THF or DME as solvent. Each time the progress of the metallation was monitored by measuring the optical spectrum of the reaction mixture between 325 and 600 nm, using a Cary 14 spectrophotometer and a quartz cell attached to the titration apparatus. The titration was stopped when excess $^-DD^-$ was present. Further experimental details of the synthesis and spectrophotometric studies will be published later.

Results and Discussion

In the early stages of the reaction, addition of $^-DD^-$ to PVFlH instantaneously generates $PVFl^-Na^+$, a polycarbanion previously reported to have been formed from the same polymer by means of sodium naphthalene for the purpose of synthesizing graft copolymers with methyl methacrylate (GOUTIÈRE and GOLÉ, 1965). Beyond about the midpoint of conversion, the reaction slows down considerably, and near the endpoint the 470 nm absorption peak of sodium $^-DD^-$ in THF persists for nearly an hour before it disappears. The peak of course remains when $^-DD^-$ is added in excess.

Prior to the endpoint the titration can be described by equation (1) and beyond the endpoint by equation (2) (AMBROZ et al, 1975).

$$VA/L = \varepsilon_{F^-}C_tV_t \qquad (1)$$

$$VA/L = (\varepsilon_{F^-}-\varepsilon_{D^-})C_tV_t^* + \varepsilon_{D^-}C_tV_t \qquad (2)$$

In these expressions, V denotes the total volume of the reaction mixture, A is the absorbance measured in a cell of pathlength L, V_t represents the volume of the added titrant $^-DD^-$ of concentration C_t, and ε_{F^-} and ε_{D^-} are the respective molar absorptivities of polymer-bound Fl^-Na^+ and of $^-DD^-$ at the wavelength used in determining the absorbance A. A plot of VA/L versus V_t at a particular wavelength λ (usually that of the absorption peak of either $^-DD^-$ or Fl^-Na^+) should yield two straight lines intersecting at V_t^*, the value of V_t at which the conversion of PVFlH into $PVFl^-Na^+$ is completed. Such a plot is shown in Figure 1 for the titration of PVFlH with sodium $^-DD^-$ in THF. Two straight lines are found resulting in a sharp endpoint when the absorbance A at 470 nm is used in the calculation. From the known amount of PVFlH and the values of V_t^* and C_t it can be calculated that the metallation of PVFlH is complete within experimental error (≈3%). The intercept on the V_t abscissa is caused by initial termination of some $^-DD^-$ by a small amount of impurity (probably water) prior to reaction with PVFlH. Its value is subtracted from the V_t value obtained for the endpoint, giving the correct V_t^*.

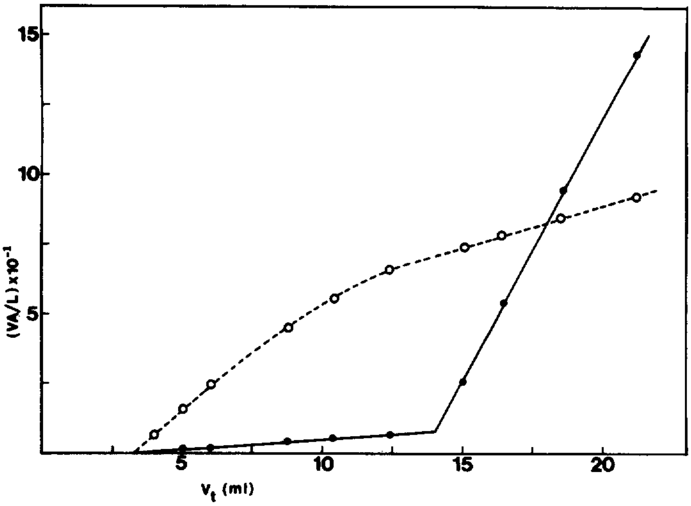


Fig. 1. Titration of poly(2-vinylfluorene) with the sodium dianion dimer of 1,1-diphenylethylene in tetrahydrofuran at 25°C. The absorbance A at 470 nm (●) and at 357 nm (O) is plotted versus the volume V_t of dianion

The plot of Figure 1 for the 357 nm maximum of $PVFl^-Na^+$ depicts a marked curvature prior to the endpoint of the reaction. In THF at 25°C, fluorenylsodium itself contains less than 5% loose ion pairs. Hence, it is not surprising that throughout the metallation process the absorption maximum of $PVFl^-Na^+$ remains at 357 nm, the maximum for the tight ion pair. However, as implied by the curved plot, the molar absorptivity of ε_{F^-} at 357 nm decreases with the progress of the metallation. This decrease is most likely the result of hypochroism caused by the close proximity of the fluorenyl chromophores. This phenomenon is quite common in polynucleotides (RICH and TINOCO, 1960) and was also observed for difluorenylbarium (TAKAKI and SMID, 1974) and for some of the fluorenyl bolaform salts (MATHIS et al, 1981). The ε_{F^-} values at low (<30%) and full metallation were calculated to be 10,000 and 7,400, respectively. The latter value is close to that found for difluorenylbarium.

When the formation of $PVFl^-Na^+$ is carried out in DME, the reaction again proceeds to completion, but this time spectral changes in the polymer-bound fluorenylsodium ion pair as a function of the degree of metallation are observed. In this solvent, fluorenylsodium itself is a loose ion pair with an absorption maximum at 373 nm, the fraction of tight ion pairs being less than 0.1 (HOGEN ESCH and SMID, 1966). Figure 2 shows that at low conversion $PVFl^-Na^+$ absorbs at 373 nm and the spectrum is essentially

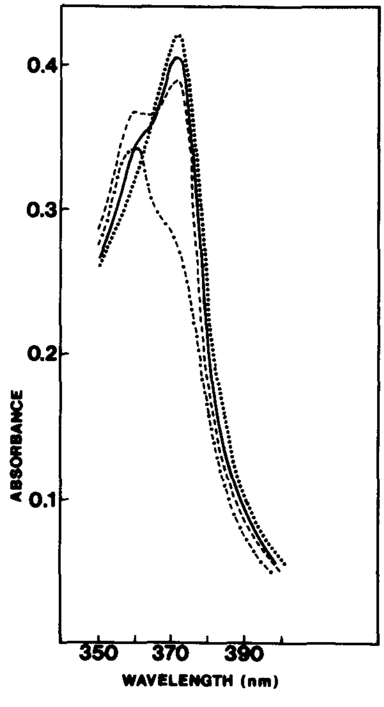


Fig. 2. Changes in the optical spectrum of poly(2-vinylfluorenylsodium) in 1,2-dimethoxyethane at 25°C as a function of the degree of conversion, a, of fluorene into fluorenylsodium. (....) a=0.5; (——) a=0.65; (---) a=0.75; (-·-) a=1.0. Spectra were normalized to $[PVFl^-Na^+]=1.9 \times 10^{-4}$

identical to that of fluorenylsodium. Above 50% conversion the 357 nm tight ion pair maximum emerges, and fully metallated PVFlH in DME at 25°C was calculated to contain a fraction 0.67 of tight ion pairs. It is also worth noting that even at 10^{-4} M concentration of polymer-bound fluorenylsodium a precipitate is formed in DME as long as the metallation of PVFlH remains below 50%. On further metallation the polycarbanion redissolves, and no precipitate or cloudiness is present when the endpoint is reached. No precipitation was observed in THF during the entire metallation process, and fully metallated PVFlH in THF can be concentrated to higher than 0.1M in carbanion without precipitation.

The occurrence of precipitation in DME during the initial stages of the metallation of PVFlH is most likely caused by intermolecular aggregation between the polymer-bound loose fluorenylsodium ion pairs. Probably because of their larger dipole moment, solvated or ligand-complexed loose ion pairs of carbanion salts have been found to aggregate easier than the corresponding tight ion pairs, causing lower solubilities (TAKAKI and SMID, 1972; HELARY et al, 1981). In THF as solvent, $PVFl^-Na^+$ remains a tight ion pair throughout the metallation, and crosslinking resulting from intermolecular aggregation is less likely. In DME, as metallation proceeds, loose ion pairs convert into tight ion pairs, thereby reducing the probability of aggregation. Also, at higher conversion, intramolecular ion pair aggregation may become the predominant mode of interaction, and this in turn will decrease polymer-polymer interactions and improve the solubility of the polycarbanion salt.

The change to a predominantly tight ion pair structure for $PVFl^-Na^+$ in DME at high degrees of metallation of PVFlH could be the result of both electrostatic and steric effects. Charge separation in the polymer-bound fluorenylsodium ion pair induced by cation-coordinating solvent molecules is energetically less favorable in the presence of an adjacent ion pair, especially when the latter is already a loose ion pair. The existence of such electrostatic effects exerted by neighboring ionic groups are of course a well-established fact in the ionization of polymers such as poly(alkali acrylates), and were also found in some of the fluorenyl bolaform salts (COLLINS et al, 1978; MATHIS et al, 1981). Not surprisingly, conductive measurements for fully metallated PVFlH yielded a degree of ionization for $PVFl^-Na^+$ in THF much lower than for fluorenylsodium itself. Loose ion pair formation at high degrees of PVFlH metallation may also be sterically hindered due to the difficulty in accommodating the required number of solvent molecules normally found around the sodium ion of a solvated loose fluorenylsodium ion pair. Moreover, increased intramolecular aggregation is likely to result in a tightly coiled polymer chain in which solvent molecules interacting with the ion pairs will be squeezed out of the polymer domain. This may be at least part of the reason for the low reactivity of this polycarbanion salt observed in preliminary protonation studies.

Low temperatures favor the solvated loose ion pair structure in carbanion salts (HOGEN ESCH and SMID, 1966), but the process is again more difficult for the polycarbanion salt. For example, equal fractions of loose and tight ion pairs are found for 10% metallated PVFlH in THF at -43°C (-33°C for fluorenylsodium itself), while at -70°C the loose ion pair fraction has reached 0.9. At this temperature the loose ion pair fraction for fully metallated PVFLH is only 0.23.

The measurements described above provide a direct way to observe and quantify changes in the solvation state of a poly ion pair in low polarity media. This type of information should be helpful in studying the reactivity behavior of such polymer systems as a function of solvent, counterion, temperature and population of the ionic reactant along the macromolecular chain.

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