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THE PREPARATION AND CHARACTERIZATION OF LINEAR AND CROSS-LINKED POLY(FLUORENYL)*

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INTRODUCTION

Retrogressive reactions in coal processing are that class of reactions that lead to the formation of high molecular weight materials that are more intractable than those present in the coal prior to processing. This outcome almost always is regarded as deleterious. The present work focuses on the characterization of the acid-catalyzed polymerization of benzylic fluorides, and in particular the synthesis of poly(fluorenyl), as an example of the type of chemistry that may occur in the cross-linked organic matrix of coals when in contact with strong acids. Solution and solid state ^{13}C NMR spectroscopy was used to characterize the soluble and insoluble polymers. The change in the value of f_a^{aH}, the fraction of aromatic carbon that is protonated[1], is the criterion used to monitor the extent of cross-linking in these polymer preparations.

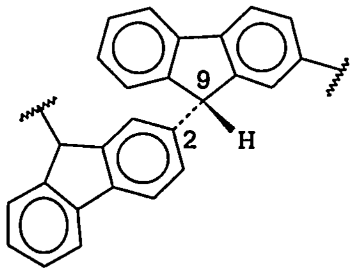
Benzylic fluorides are sensitive substances, prone to further reaction via acid catalyzed heterolytic scission of the C-F bond. The electron deficient reactive intermediate formed in this reaction undergoes electrophilic aromatic substitution. This reaction can be started with catalytic traces of acid and is self- sustaining as HF is generated in equivalent concentrations as the reaction proceeds. The relevance of this naturally non-occurring functional group in coal processing stems from the similar reaction pathway followed by both benzylic fluorides and benzylic alcohols. In the coal matrix, the operation of two exogenous processes- air oxidation and strong acid treatment of the coal (demineralization) creates a situation in which the polymerization discussed herein may occur in the coal. In addition to the polymerization reactions that produce poly(fluorenyl), the subsequent cross-linking of the linear polymer is also reported. In subsequent work, similar chemistry will be applied to soluble lignin as a model more similar to low rank coals.

RESULTS AND DISCUSSION

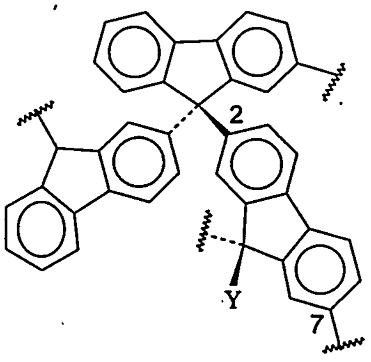
The generation of poly(fluorenyl), PF, is most easily effected by impurity- or self-catalyzed decomposition of solid 9-fluorofluorene. The solid state reaction proceeds unattended by storing the monomer in a closed, dry glass container at room temperature. In a matter of days the white, crystalline 9-fluorofluorene is completely converted into a white, fluorine-free, *soluble* polymer. This material is identical (except in molecular weight distribution) to the polymer generated from 9-fluorofluorene in hexane or THF solution that has been treated with catalytic trifluoroacetic acid. A polymer that is virtually indistinguishable from that derived from 9-fluorofluorene is obtained from the reaction of 9-hydroxyfluorene in HF/pyridine.

The gross structure of the polymer follows from the change in f_a^{aH} between the monomer, 9-fluorofluorene (0.67 ± 0.02) and the polymer (0.59 ± 0.02), i.e., a change from 8 to 7 aromatic methines out of 12 aromatic carbons. The identification of protonated and non-protonated aromatic carbon resonances is made through dipolar dephasing experiments.[2] In Figure 1 the two resonances with chemical shifts greater than 140 ppm represent the non-protonated aromatic carbons in this polymer. In addition, the C(9) fluoromethine resonance (92.6 ppm, $^1J_{CF}$ = 180 Hz) of 9-fluorofluorene is absent in the polymer. Indeed, no fluorocarbon resonance appears in the polymer.

The tetrahedral carbon resonance in the polymer occurs at 54.5 ppm (Figure 1a). These data indicate the loss of the carbon-fluorine bond and the formation of a carbon-carbon bond between C(9) and an aromatic carbon of another fluorene moiety. The C(9) resonance of the model 9-phenylfluorene is 54.4 ppm, an excellent match for the corresponding resonance in the polymer. The site of attachment of C(9) of one residue to the aromatic ring of the next monomer unit is C(2) [see the structure for numbering]. This attachment is supported by (1): chemical shift additivity arguments, (2): the well established electrophilic substitution pattern observed in fluorene, e.g., nitration of fluorene produces solely 2-nitrofluorene, and (3): a proof of structure based on long range ^{1}H-^{13}C coupling in 2-(pentamethylbenzyl)fluorene, prepared by the acid-catalyzed reaction of pentamethyl benzyl fluoride with fluorene. The polymer has the structure shown below labeled linear PF, *l*-PF. The line widths of the resonances in the solid state spectrum are on the order of 125 Hz. The high resolution ^{13}C NMR spectrum of this highly soluble *l*-PF, obtained at low concentration in $CDCl_3$ to keep solution viscosity low, shows an order of magnitude better resolution than the solid state spectrum. The spectrum contains evidence of conformational heterogeneity of the polymer, with most carbons represented by a narrow manifold of chemical shifts that produces an asymmetric or split resonance band shape. This distribution in chemical shifts is too small to be an indication of the presence of structural isomers.



l-PF



t-PF

The *l*-PF formed from the solid state reaction of 9-fluorofluorene has a number average molecular weight, $M_N = 568$ and polydispersity, $M_W/M_N = 2.5$ determined by GPC. The weight average molecular weight, 1420, is in good agreement with that determined from end group analysis in the solid ^{13}C NMR spectrum, 1245. The end group resonance in this spectrum occurs at 36.0 ppm, the chemical shift of C(9) in the fluorene itself. It is possible that the polymer could bite back on itself, generating a ring or branch point in the polymer. The linkage so generated would be indistinguishable from the linear C(9) polymer resonances on the basis of chemical shift. Such structures, if present in high concentration would be reflected in low $f_a^{a,H}$ values.

Treatment of *l*-PF with F-TEDA or with HF/pyridine/$NO^{+}BF_4^{-}$, reagents used to introduce a fluorine substituent at unactivated aliphatic sites, fails to generate the intended product, poly(9-fluorofluorenyl). The products are *fluorine-free*, have a ^{13}C NMR spectrum similar in appearance to the starting material (cf. Figure 1a,b), and are *highly insoluble.* Integration of the aromatic resonances reveals $f_a^{a,H} = 0.56 \pm 0\ 020$.[3] These facts indicate that the polymer has been cross-linked by this chemical treatment. The implication is that the reagents do in fact generate the 9-fluoro *l*-PF, but that this product, like the 9-fluoro monomer, undergoes cationic polymerization. The $f_a^{a,H}$ of the product indicates that one of every three fluorenyl residues in the product, *t*-PF, has a new intra- or inter-chain C(9)-C(2) connection. The statistical repeating structural unit of *t*-PF is shown above. In the limit of complete cross-linking the aromatic CH/C ratio would become 6/6, i.e., $f_a^{a,H}$ = 0.50. The inter-chain cross-links imbue the polymer with its high insolubility. All samples of *t*-PF that we have synthesized are cross-linked to about the same extent ($f_a^{a,H} = 0.55 \pm 0.02$). This may represent a limiting degree of polymerization dictated by the physical constraints of the polymer chain. In addition to the 54 ppm resonance representing mono- and di-aryl substituted C(9) carbons of the fluorenyl residues, a new resonance at 83 ppm appears in the spectrum of *t*-PF produced using F-TEDA (Figure 1b). This is the region of the spectrum for oxygenated aliphatic carbon resonances. The resonance represents the incorporation of 9-aryl-9-fluorenol residues in the *t*-PF polymer (Y = OH in the above structure). The C(9) resonance of the model, 9-phenyl-9-hydroxyfluorene, is 83.4 ppm. This functionality likely arises from quenching of fluorenyl cation sites with water during reaction work-up, sites that can not react by the usual pathway due to physical constraints built into the cross-linked polymer.

REFERENCES

1. M. A. Wilson, R. J. Pugmire, J. Karas, L. B. Alemany, W. R. Woolfenden, and D. M. Grant, *Anal. Chem.*, **56**, 933, (1984).

2. P. D. Murphy, B. C. Gerstein, V. L. Weinberg, and T. F. Yen, *Anal. Chem.*, **54**, 522, (1982).

3. The error limits on the aromaticity determinations reflect the absolute error in this quantity. The theoretical value of $f_a^{a,H}$ for the linear polymer is 0.583. The value from the direct NMR integral, splitting the area at the saddle point, is 0.60. Peak fitting with an assumed Gaussian line shape yields 0.59, while allowing the line shape to be treated as a mixed Gauss-Lorentz line produces the best line fit (smallest residuals) and a value of 0.61. The ± 0.02 error limits reflect these uncertainties as well as the deviations from linear response that may accrue in the actual experiment. However, in comparisons between two similar materials, taking care to use the same evaluation criterion for both, the relative error is small. The 0.03 difference in $f_a^{a,H}$ between *l*-PF and *t*-PF is reproducible, indicating a small relative error.

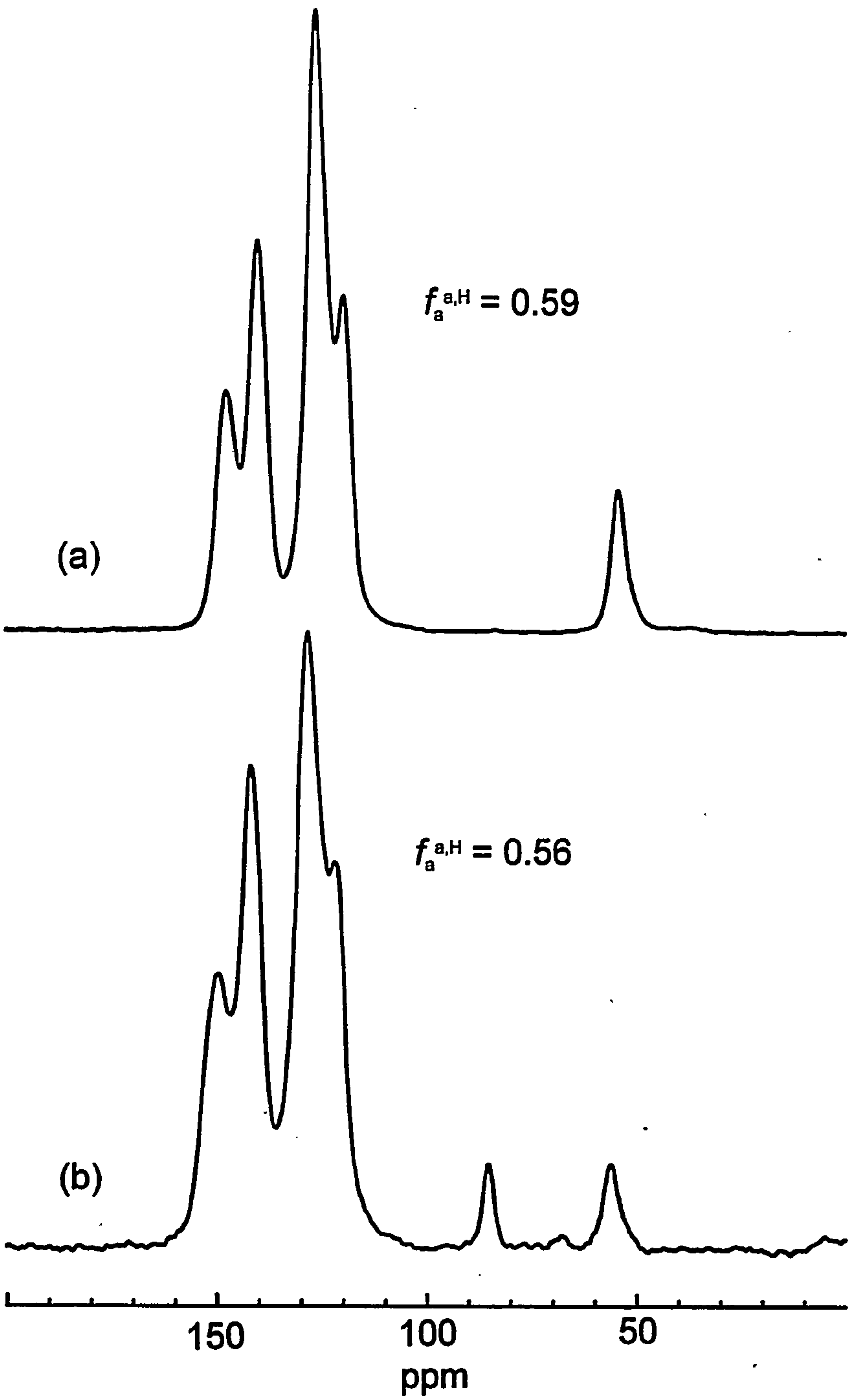


Figure 1. ^{13}C NMR spectra of (a) *l*-PF from the solid state polymerization of 9-fluorofluorene and (b) *t*-PF from the reaction of l-PF with F-TEDA. Broadening of the aromatic peaks in 1b relative to 1a and the change in $f_a^{a,H}$ evidence the increase in conformational heterogeneity and cross linking in *t*-PF. The $f_a^{a,H}$ values are calculated from areas derived from peak deconvolution of the aromatic resonances.