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The influence of H-bonding in liquid crystalline polyazomethine ethers

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Summary

The model compound 1,4-bis(anisylimido)benzene has been characterized by solution and CP/MAS ^{13}C NMR to assist in the characterization of liquid crystalline polyazomethines (PAM) based on the same mesogenic structure. Thermal behavior of several homologs of this PAM series have been compared before and after treatment with the end capping agent benzaldehyde. The results suggest that PAM oligomers containing large quantities of amine termination can strongly effect thermal behavior at constant oligomer molecular weight.

Introduction

Cross polarization/magic angle spinning (CP/MAS) NMR has become a very useful tool for the structural and conformational analysis of liquid crystalline polymers (LCP) (1-4). This technique has assisted in determining the repeat structure of insoluble polymers. Yet nearly all of LCP studied have involved polyesters and have concentrated upon the conformational changes of the polymer within and during phase changes. The PAM type of LCP although having found renewed interest have not generally been well characterized (5-10). We have become interested in understanding the influence of chain end nature upon LCP properties, especially oligomers. H-bonding phenol termination has been shown to dramatically impart changes to thermal behavior of LCP polyethers (11). The question is then raised: can amine termination in PAM oligomers influence thermal behavior? The directive of this work is to begin to address this question by structurally and thermally characterizing oligomeric PAMs.

Experimental

The synthesis of the model compounds and α,ω-bis(4-formylphenylene oxy)alkanes (M_1) are presented in detail elsewhere (12). Polymerizations between M_1 and phenylene diamine were carried out at 1:1 stoichiometry with piperidine as catalyst in refluxing toluene. Reactions were carried out for two days. End-capping reactions were carried out in situ as well as post polymerization. In both cases, a 1.2 molar excess per repeat unit of benzaldehyde was added at reflux and the reaction was allowed to continue for an hour before work-up. Polymers were cleaned up with methanol and dried in vacuo. Detailed examples of these procedures are presented elsewhere (12). ^{13}C NMR (75.5 MHz) spectra were recorded on a Bruker MSL 300. Solution NMR was performed in $CDCl_3$ at 50 °C using the residual chloroform peak at 77.0 ppm as an internal standard. CP/MAS NMR spectra were recorded at 10 KHz or greater spinning speeds (Doty Scientific Inc. probe) in order to eliminate side band interference. The methide carbon of adamantane (28.35 ppm) was used as a reference standard. Thermal behavior was

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recorded with a DuPont 9900 Thermal Analysis Data Station. Other analysis methods ascribed to standard techniques.

Results and Discussion

Structural characterization of PAM polymers can be best accomplished by establishing a data set with a model compound. In this case, 1,4-bis(anisylimido)benzene best approximates the mesogen used in this study. Figures 1 and 2 show the solution and solid state NMR spectrum of this model.

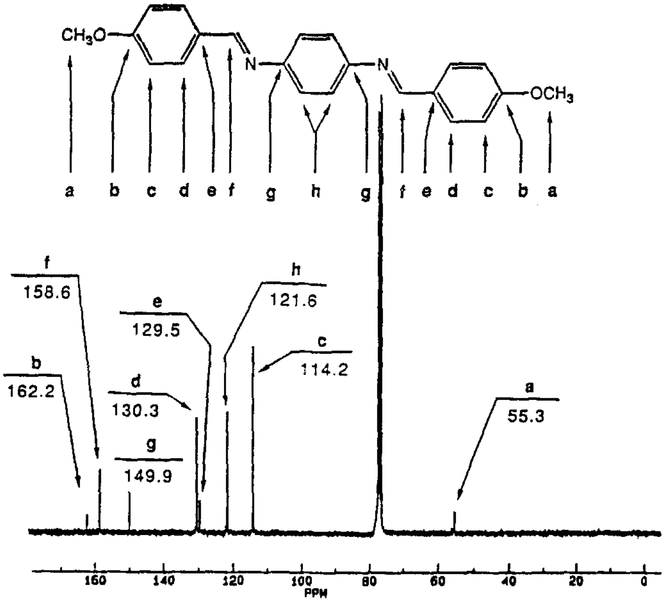

Figure 1: 75.5 MHz ^{13}C NMR ($CDCl_3$) spectrum of 4-bis(anisylimido) benzene, model for the PAM polymers.

The solution spectrum permits assignment of resonances to structure as shown in Fig. 1. Correlation with the CP/MAS spectrum is quite good, but it has two distinguishing features. First, relative intensity levels of each resonance are not in relative proportion to those in Fig. 1. This is not unexpected (13). Note however the splitting of the resonances center about 158 and 149 ppm. Splitting of this order is often attributed to conformational effects and non-equivalent crystal lattice sites. Additional work with x-ray diffraction will be necessary to completely clarify its origin. Confirmation of the assignments in the CP/MAS spectrum were assisted by a magnetic defocusing experiment where only contributions from quaternary aromatic carbons are observed (14). The technique is ineffective for aliphatic carbons. The results of this experiment are shown in Fig. 3. Clearly the quaternary carbons b,e and g are assigned properly.

Despite these few distinguishing features, the model compound has provided a good data base for characterization of the polymers. Only two polymers will be considered here. These polymers were prepared in toluene. The same structures were prepared in an earlier report in which the authors utilized ethanol (7). These solvents may generate polymers with different chain end structures. Both polymers

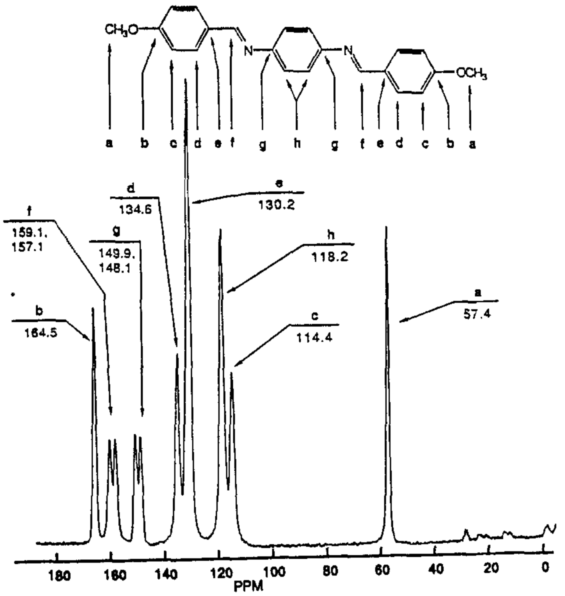

Figure 2: 75.5 MHz ^{13}C CP/MAS NMR spectrum of 1,4-bis(anisylimido) benzene.

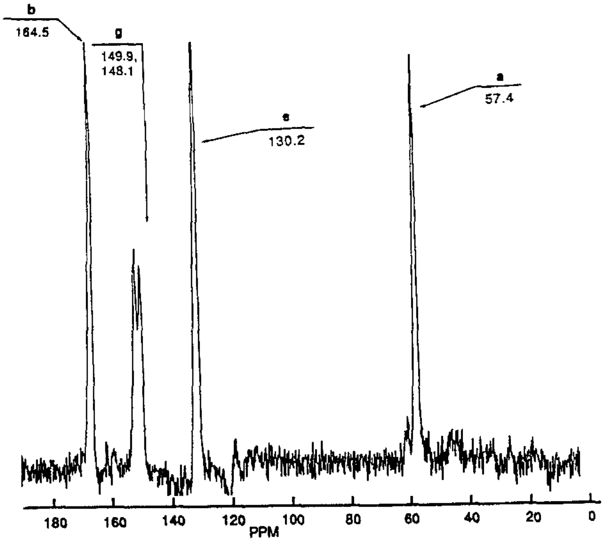

Figure 3: 75.5 MHz ^{13}C CP/MAS magnetic defocussing NMR spectrum of 1,4-bis(anisylimido) benzene.

were prepared with and without an end capping step utilizing benzaldehyde to remove amine termination. Fig. 4 shows an example CP/MAS NMR of a polymer isolated without end capping. NMR spectra for all polymers samples were recorded on "as precipitated" samples. The thermal history of these samples did not appear to influence the resulting spectra; although it is known that thermal history can affect changes in NMR spectra (1-4). Two differences are noted in comparison with the model spectrum. First, the split signals do not appear split in the spectra of the polymers. This may suggest an equivalency in the environment around this structure in the polymer. Several aromatic signals are not accounted for by the repeat unit alone (114.4, 124.6, and 134 ppm). They do, however, correspond to aminophenyl end groups. FTIR spectroscopy corroborates this finding with a large broad band between 3356 and 3174 cm^{-1} (N-H symmetric stretch) as well as bands at 1605 and 815 cm^{-1} (primary N-H bend). Both of these findings change with the added end capping step. N-H bands in the IR spectrum disappear and, as seen in Fig. 5, the aminophenyl resonances are replaced with phenylimine resonances.

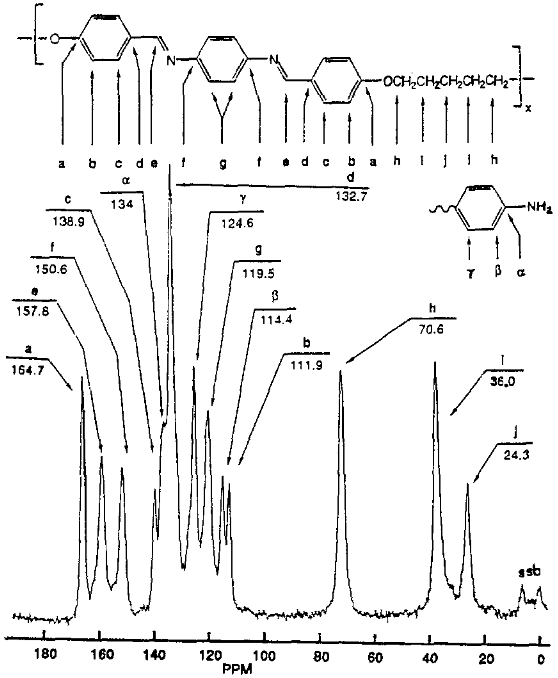

Figure 4: 75.5 MHz ^{13}C CP/MAS NMR spectrum of PAM-5 as precipitated from the reaction.

With these changes in structure noted, we turn to the physical properties of these polymers. The addition of the end capping step did not seem to influence molecular weight, but it had a remarkable effect upon the thermal properties (Table).

			Thermal Transition on Heating (°C)					
	IV (dl/g)		T_g		T_{m1}		T_{m2}	
n	native	ec	native	ec	native	ec	native	ec
5	0.42	0.42	---	---	dec.	283	---	290
9	0.38	0.38	---	153	252	---	268	257

ec = endcapped

IVs recorded on trifluoromethanesulfonic acid solutions were the same for polymers before and after performing the end capping step (for both in situ and post polymerization end capping). Currently IV is the only method for which to record

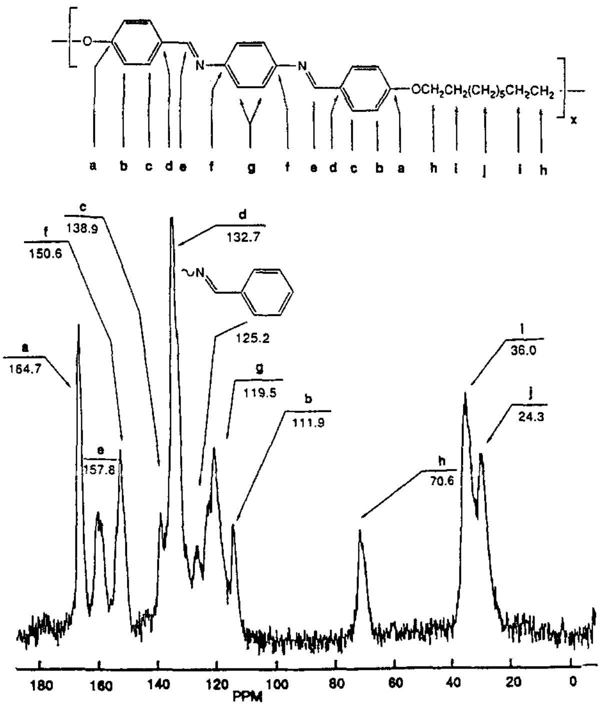

Figure 5: 75.5 MHz ^{13}C CP/MAS NMR spectrum of PAM-9 after endcapping with benzaldehyde.

molecular weight of these highly insoluble materials. Even so it appears that the addition of benzaldehyde serves to remove the amine termination without radically altering molecular weight. Hence we may compare the thermal properties with and without amine termination at approximately the same chain length. The thermal properties for each polymer changed upon removing the H-bonding amine. With amine termination PAM 5 decomposed with out melting. Yet with neutral termination the same polymer melted into a birefringic melt (for discussion of possible phase behavior and texture see (7) and (11)). Pam 9 gave only a broad melting endotherm with overlapping peaks. With neutral termination the polymer responded with a crisp T_g and a narrow well defined endotherm. One could conjecture that the two endotherms recorded for amine terminated PAM 9 might be due to oligomeric fractionation resulting from degrees of H-bonding. Although we can record the presence of amine termination, we have not quantified the amount of amine termination per sample.

Comparison of our data with those before is difficult because of the tentative nature of the IV determination. This is largely due to the relative instability of these polymers in trifluoromethanesulfonic acid. Some decomposition is inherent. In this context, the work presented here suggests a cause of the variability in thermal data for PAM among research groups: hydrogen bonding. For instance, PAM 5 is reported to decompose over 350 °C without melting (7). For similar molecular weight, the PAM 5 prepared here performed the same until amine termination was removed. A similar trend is noted for PAM 9 which is reported to exhibit two endotherms at 240 and 370 °C (7). Removal of amine terminated effected a reduction in the number and greatly improved the resolution of the endotherm.

Acknowledgements

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