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^{1}H and ^{13}C NMR Spectroscopic Characterization of Poly(amide−enaminonitriles)

J. A. Moore*,† and Sarjit Kaur‡

Department of Chemistry, Rensselaer Polytechnic Institute, Troy, New York 12180-3590 and Department of Chemistry, Vassar College, Poughkeepsie, New York 12604-0287

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ABSTRACT: ^{1}H and ^{13}C NMR spectroscopy was used to characterize regularly alternating copolymers, poly(amide−enaminonitriles), using 1D and 2D NMR experiments (HMQC and TOSCY) and NMR spectroscopic data of closely related model compounds. Copolymers from the condensation of an unsymmetric diamine, 4,4′-diaminobenzanilide, with 1,3- or 1,4-bis(1-chloro-2,2-dicyanovinyl)benzene were determined to be predominately ordered polymers, with ~85% of the structures containing head-to-head/tail-to-tail arrangements. The microstructural features of these polymers were determined using ^{1}H NMR spectroscopy where peaks representing head-to-head and tail-to-tail distributions were identified by comparison to a model compound and regularly alternating copolymers that had strictly head-to-head or tail-to-tail compositions.

Introduction

One of the many approaches used to improve solubility of aramids includes a direct modification of the amide bond. This modification is based on an observation made by Wallenfels[1] who noted that the $=C(CN)_2$ group is inductively equivalent to an oxygen atom. The modified amide linkage, $NH-C=C(CN)_2$, which we have called enaminonitrile, exhibits resonance, dipolar and hydrogen bonding features that are similar to those characteristic of the amide bond. A series of homopolymers containing the $NH-C=C(CN)_2$ moiety, poly(enaminonitriles), have been prepared as high molecular weight materials and these exhibit significantly improved solubility over aramids in ordinary laboratory solvents such as glyme, dimethylformamide, dimethylacetamide, and dimethyl sulfoxide.[2] Recently, we have also reported the synthesis of high molecular weight copolymers containing both the amide and enaminonitrile moieties, poly(amide−enaminonitriles).[3] These copolymers show comparable solubility and thermal properties to homopoly(enaminonitriles) even when 50% of the functional moieties are amide linkages. In this paper, we report the detailed ^{1}H and ^{13}C NMR spectroscopic characterization of the regularly alternating poly(amide−enaminonitriles), and those from the condensation of an unsymmetrical amine, 4,4′-diaminobenzanilide, and 1,3- or 1,4-bis(1-chloro-2,2-dicyanovinyl)benzene.

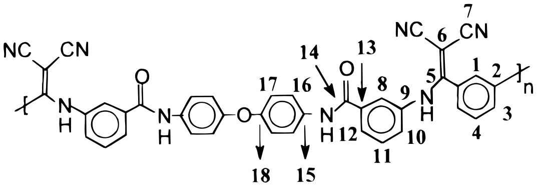
With 4,4′-diaminobenzanilide, the polymerization is initially expected to proceed from the reaction of the more reactive amino group (the one para to NH; head group), suggestive of some degree of order in the copolymer. Further, the polymerization was carried out by slow addition of the monomers, 1,3- or 1,4-bis(1-chloro-2,2-dicyanovinyl)benzene,[4] to a solution of 4,4′-diaminobenzanilide, a strategy reportedly leading to highly ordered copolymers when an unsymmetrical monomer is used.[5−7] Definitive peak assignments of these copolymers, using 2D NMR spectroscopy and comparison to other appropriate regularly alternating copolymers, made it possible to deduce the degree of order achieved by determining the microstructural distribution (head-to-head/tail-to-tail vs head-to-tail) in these copolymers.

Experimental Section

The synthesis and properties of all model compounds and polymers described in this paper have been reported previously.[3] Nuclear magnetic resonance (NMR) spectra were recorded on a Varian 500 (500 MHz ^{1}H; 125 MHz ^{13}C) spectrometer. The NMR shifts were recorded as parts per million (ppm) and are referenced to residual solvent resonances of dimethyl-d_6 sulfoxide. The experimental ^{13}C chemical shifts were compared to calculated values for the aromatic region.[8] The parameters used for the 2D ^{1}H−^{1}H (TOCSY) NMR experiments were as follows: spectral width of 1250 Hz, pulse width of ~10 μs; mixing time of 0.045 s; relaxation delay of 0.6 s, acquisition time 0.4533 s. The parameters used for the 2D ^{1}H−^{13}C (HMQC) NMR experiments were as follows: ^{1}H spectral width of 1250 Hz; ^{13}C spectral width of ~2000 Hz; pulse width of ~10 μs; acquisition delay 0.4 s; acquisition time 0.096 s; mixing time of 0.045 s; relaxation delay of 4 s.

Results and Discussion

NMR Characterization of Regularly Alternating Poly(amide−enaminonitriles). ^{1}H NMR spectra of model compounds and poly(amide−enaminonitriles) exhibited broad, overlapping peaks in the aromatic region while ^{13}C NMR spectra showed a complex pattern of aromatic peaks. Representative examples of ^{1}H and ^{13}C spectra are shown for copolymer **A** in Figures 1 and 2, respectively. The high molecular weight of the copolymers caused relatively viscous solutions in deuterated dimethyl sulfoxide, even at 2−3% solutions. The



Copolymer **A**

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† Rensselaer Polytechnic Institute

‡ Vassar College.

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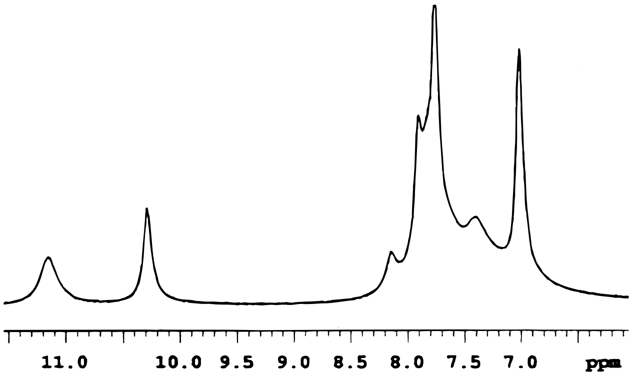


Figure 1. ^1H NMR spectrum of copolymer **A** at room temperature.

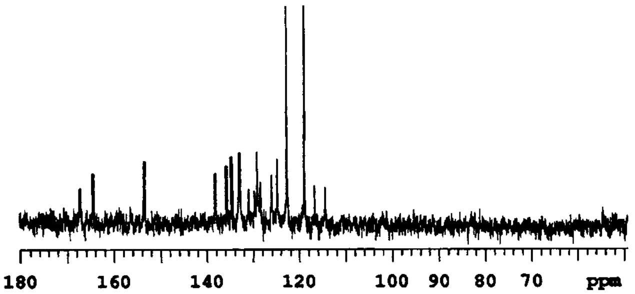


Figure 2. ^{13}C NMR spectrum of copolymer **A**.

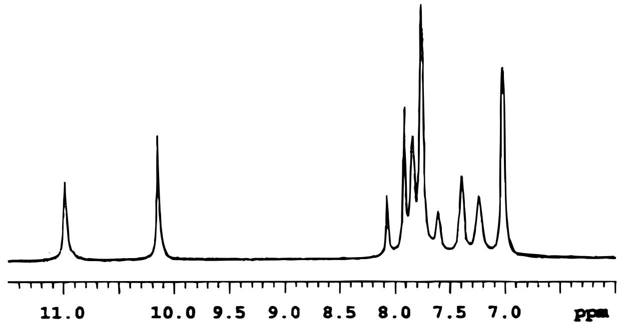


Figure 3. ^1H NMR spectrum of copolymer **A** at 60 °C.

broadness of the peaks in the ^1H NMR spectra can be the result of a number of factors: low tumbling rates of macromolecules because they are large molecules and the higher viscosity of polymer solutions relative to solutions of small molecules.[9] Additionally, rotational barriers exists both in the amide and enaminonitrile C−N bonds and several geometric isomers are possible.[10] These are likely to have slightly different chemical shifts that are not clearly resolved in the aromatic region, giving the appearance of broad peaks. At higher temperatures, the solution viscosity decreases and the tumbling rates of large molecules increase, both factors resulting in narrower peaks. For these reasons, the NMR analyses were carried out between 60 and 70 °C, temperatures that would also overcome the barrier to rotation where a fast exchange between the geometric isomers would lead to fewer and resolved peaks (only the average resonance of different geometric isomers would be observed). Figure 3 shows the results of the^1H NMR experiment for copolymer **A** carried out at 60 °C. The spectrum shows resolved and narrower peaks that are more amenable to characterization than those of Figure 1.

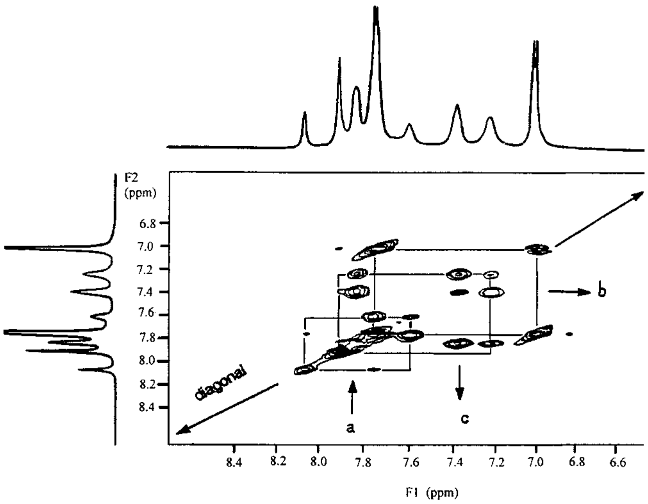


Figure 4. TOCSY NMR ($^1H-^1H$ correlation) spectrum of copolymer **A** at 60 °C.

The complex number of peaks seen in the aromatic regions dictated the use of 2D NMR experiments for characterization of as many peaks as possible. Heteronuclear multiple-quantum coherence (HMQC) and total correlation spectroscopy (TOSCY) NMR experiments were employed to determine $^1H-^{13}C$ and $^1H-^1H$ correlation, respectively.[8] The combination of these two NMR experiments enabled the assignment of most peaks, along with corroborating information obtained from model compounds, previously reported results and calculated carbon values. The discussion that follows outlines the interpretation of NMR data for selected polymers. Data on ^1H and ^{13}C peak assignments of other poly(amide−enaminonitriles) and model compounds has been reported in an earlier publication.[3]

The TOCSY NMR experiment correlates protons that are coupled to each other through short and long range coupling; it is especially useful in identifying coupled proton resonances that originate from a given residue in proteins. For poly(amide−enaminonitriles), coupling was present only between protons of the same benzene ring, allowing resonances for a given ring to be identified. The results of the TOCSY experiment for copolymer **A**, conducted at 60 °C, are shown in Figure 4 where the proton resonances that are coupled to each other are outlined with a box drawn around them; three sets of coupled resonances were identified (a, b, and c), each corresponding to a given benzene ring in the repeat unit of copolymer **A**. The resonances found coupled to each other were differentiated further using splitting patterns and integration areas. On the basis of the 2:1 integration ratio observed for the singlets at 7.92 and 8.01 ppm, were assigned to H_8 and H_1, respectively, where H_1 is expected to be more downfield because it is flanked by two electron withdrawing dicyanovinylidene groups. The other coupled peaks to H_1 (box “a”), 7.60 and 7.75 ppm, are assigned to H_4 and H_3, respectively, because integration of H_4 corresponds to one proton and is expected to be upfield from H_3, being meta to two dicyanovinylidene groups. H_3 is found overlapping with another peak (7.75 ppm) that is part of box “b”. In box “b”, the doublet at 7.0 ppm corresponds to four protons by integration and is assigned to H_{17}. H_{17} is ortho to an electron-donating group (an oxygen atom) and would be expected to be shifted upfield as compared to H_{16}, which can be assigned to 7.75 ppm by default.

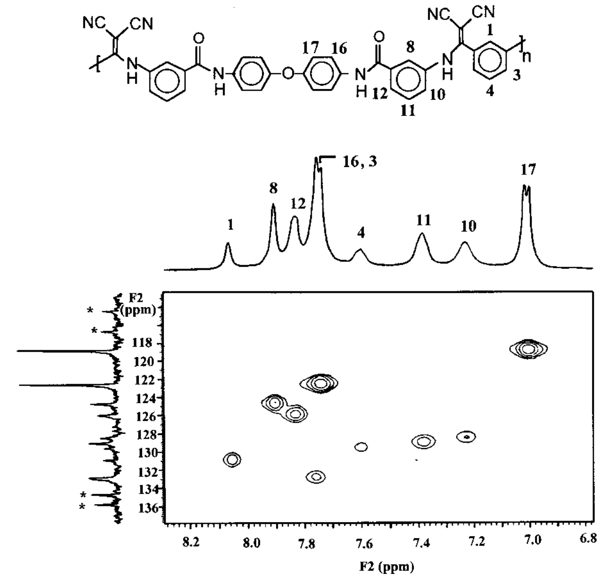


Figure 5. HMQC NMR ($^1H-^{13}C$ correlation) spectrum of copolymer **A** at 60 °C.

Table 1. ^{13}C NMR Assignments for Copolymer A[a]

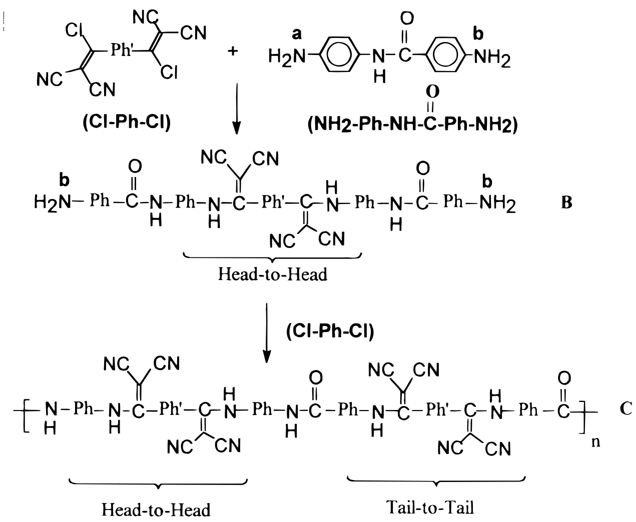
carbon	calculated shift, ppm[b]	measured shift, ppm	basis of assignment
1	128.7	130.8	HMQC/TOCSY
2	137.6	135.7 or 138.0	calculation
3	132.8	132.8	HMQC/TOCSY/calculation
4	128.5	129.5	HMQC/TOCSY
5		167.1	*e*
6		55.0	*e*
7		114.3, 116.1	*e*
8	118.7	124.6	HMQC/TOCSY
9	139.6	*c*	*e*
10	122.8	128.4[d]	HMQC/TOCSY
11	128.7	129.0[d]	HMQC/TOCSY
12	123.0	125.9	HMQC/TOCSY
13	137.8	135.7 or 138.0	calculation
14		164.4	*e*
15	134.5	134.6	calculation
16	120.2	122.5	HMQC/TOCSY/calculation
17	119.2	118.8	HMQC/TOCSY
18	152.1	153.3	calculation

[a] Done in deuterated dimethyl sulfoxide. [b] $CH_3-C=O$ was used instead of $C=C(CN)_2$. [c] Not observed because it is weak or possibly hidden by another peak in the aromatic region. [d] Tentative assignments. [e] Comparison to previously reported data.[2]

Box "c" includes the singlet at 7.92 ppm (already assigned to H_8) and three other resonances at 7.20, 7.40, and 7.88 ppm. H_{12} is assigned to 7.88 ppm because it is a doublet, shows two protons by integration and is expected to be more downfield than H_{10} and H_{11} because of ortho substitution to a carbonyl group. The distinction between H_{10} and H_{11} is less conclusive. Although H_{10} is expected to be a doublet and H_{11} a triplet, both are seen as relatively broad peaks (7.20 and 7.4 ppm). A closer examination of the peak at 7.4 ppm appears to indicate a possible triplet and, on this basis, tentative assignments of these two peaks are made (H_{11} at 7.4 ppm and H_{10} at 7.2 ppm).

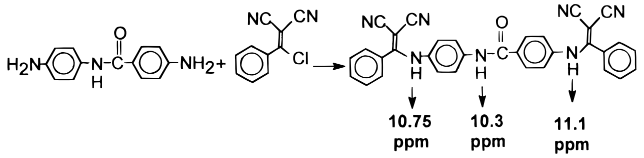
On the basis of the preceding assignments of proton peaks, the assignment of ^{13}C peaks bearing protons was made using data from HMQC NMR experiments. The results of an HMQC NMR experiment conducted on polymer **A** are shown in Figure 5 and these results are tabulated in Table 1, along with the calculated results of ^{13}C peaks. The proton peak at 7.75 ppm shows two ^{13}C resonances at 132.8 and 122.5 ppm; these are assigned to C_3 and C_{16}, respectively, by comparison to their clearly distinguishable calculated values. There was generally good agreement between experimental and calculated values for ^{13}C assignments, showing consistent trends, as seen for C_1, C_3, C_4, C_{11}, C_{12}, C_{16} and C_{17}. Although C_8 and C_{10} were not as close, the relative trends with respect to each other and the other assignments were consistent. Peak resonances corresponding to carbons with no attached protons (those not observed on HMQC) were assigned by comparison to calculated values (C_2, C_{13}, C_{15} and C_{18}) and comparison to previously reported assignments (C_5, C_6, C_7, C_9 and C_{14}).[2] C_2 and C_{13} were not distinguishable because their calculated values were too close.

Scheme 1. Synthesis of Poly(amide−enaminonitriles) from 4,4′-Diaminobenzanilide



Structural Characterization of Copolymers made from 4,4′-Diaminobenzanilide using ^1H NMR Spectroscopy. In the polycondensation of 4,4′-diaminobenzanilide (H_2N-**a**$-$**b**$-NH_2$) with 1,3- or 1,4-bis(1-chloro-dicyanovinyl)benzene (Cl−Ph′−Cl), the amino group para to the electron-donating NH group (**a**, head group) is more reactive than the amino group para to the carbonyl group (**b**, tail group). The initial condensation is expected to proceed via reaction of the more reactive amino group (**a**) if Cl−Ph′−Cl is added slowly to a solution of the diamine,[4] the latter being in excess initially. As shown in Scheme 1, the initial adduct is a symmetrical diamine containing a head-to-head arrangement (**B**). Once all the head amino groups have reacted, further addition of Cl−Ph′−Cl can only lead to reaction of tail groups (**b**) and, as a result, an ordered polymer with regularly alternating sequences of head-to-head and tail-to-tail arrangements is expected. The reaction of 4,4′-diaminobenzanilide with 1,3 or 1,4-bis(1-chloro-dicyanovinyl)benzene gave copolymers **G** (meta-substituted) and **C** (para-substituted), respectively. A model compound (**D**) was prepared by condensation of 4,4-diaminobenzanilide with 1-chloro-dicyanovinylbenzene to determine NH proton resonances. The ^1H NMR shifts of the NH groups in the model compound are shown in Scheme 2. The enaminonitrile NH peak resonances are typically found 0.7−1.0 ppm higher than the amide peak.[11] Thus, the amide proton of model compound **D** is assigned to the resonance at 10.3 ppm, and is not expected to shift appreciably with structural changes para to it (head-to-head vs tail-to-tail configu-

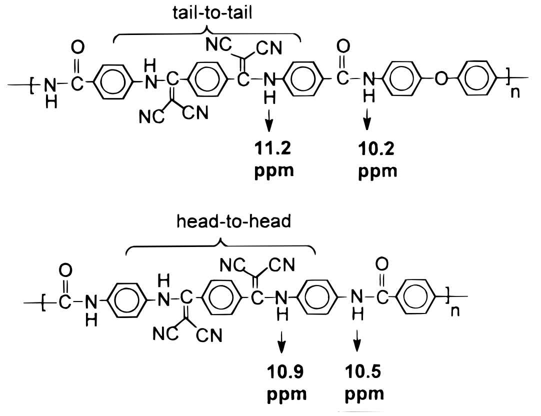
Scheme 2. Synthesis of Model Compound D



D

Scheme 3. Proton Peak Resonances of NH Region for Copolymers E and F

E



F

rations). The most downfield peak at 11.1 ppm is assigned to the amino group found para to the carbonyl group, leading to the assignment of the remaining NH to the peak at 10.75 ppm (Scheme 2). Besides these deductions, proton resonances for NH$-$(C$=$C(CN)$_2$ representative of head-to-head and tail-to-tail orientations can also be obtained from ^{1}H NMR spectra of two regularly alternating copolymers that contain only head-to-head configuration (polymer **F** showing NH(C$=$C(CN)$_2$ at 10.9 ppm) or only tail-to-tail configuration (polymer **E** showing NH(C$=$C(CN)$_2$ at 11.2 ppm) (Scheme 3).

The ^{1}H NMR spectra of the model compound and polymer **C** are shown in Figure 6. The broad peaks (**e**) found at 10.35, 10.85, and 11.2 ppm for polymer **C** correspond closely to those of the model compound, strongly suggesting a predominance of head-to-head and tail-to-tail configurations. The narrow peaks (**f**) present at 10.2, 11.1, and 11.35 ppm are suggestive of a different polymer distribution than the broad set of peaks. These peaks are believed to be low molecular weight materials because the presence of two doublets at 6.80 and 6.90 ppm are suggestive of end-group resonances. Although the NMR data strongly suggest a predominantly ordered **C** polymer, the general broadness of the NH region could have hidden the NH proton resonances representative of head-to-tail configuration, expected to lie between 10.75 and 11.2 ppm and in small proportion. ^{1}H NMR experiments carried out at higher temperatures of ~60 °C did not significantly improve the resolution or broadness of the NH region. Consequently, a different region was identified that did not depend on an acidic proton such as NH. Polymer **G**, from the polycondensation of 1,3-bis(1-chloro-2,2-dicyanovinyl)benzene with 4,4′-diaminobenzanilide, was selected because its ^{1}H NMR and GPC data showed negligible amounts of end groups and the 1,3-substituted benzene showed a distinct region (8.0$-$8.25 ppm) in the ^{1}H NMR spectra that reflected changes in the polymer configurations. The aromatic proton found ortho to two dicyanovinyl groups (H$_1$) was assigned to this region, using TOCSY and HMQC 2D experiments. The integration of this region gave the equivalent of one proton relative to the other aromatic protons and represented contributions only from H$_1$. For copolymer **G**, three distinct resonances were identified between 8 and 8.25 ppm (Figure 7), each representing a slightly different environment for proton H$_1$. To obtain more information regarding the assignment of these three peaks, the same aromatic peak (H$_1$) in copolymer **H** was seen as a singlet at 8.16 ppm, identified through TOCSY/HMQC 2D NMR experiments, and is representative of a tail-to-tail configuration (see Figure 8). Another copolymer, **I**, shows H$_1$

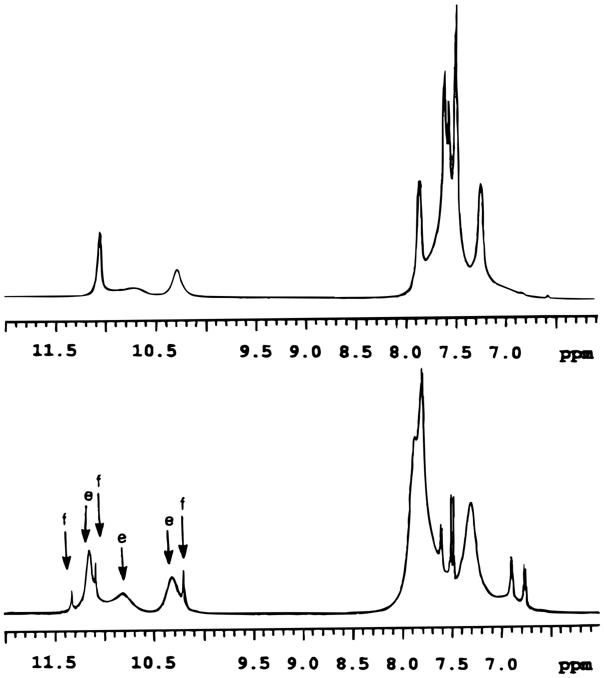
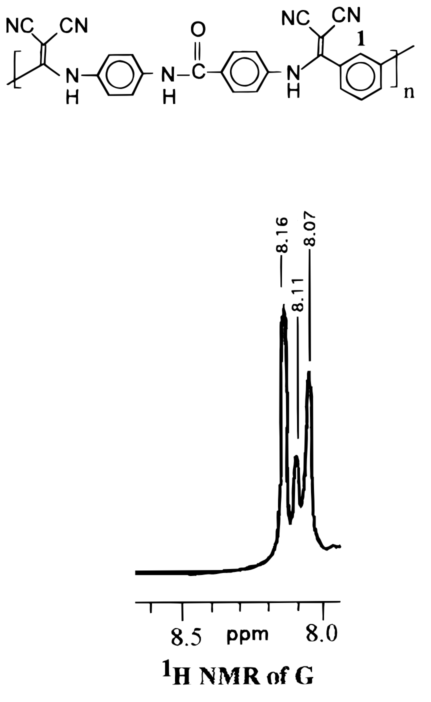


Figure 6. ^{1}H NMR spectra of the model compound **D** (top scan) and polymer **C** (bottom scan).



G

Figure 7. Repeat unit and ^{1}H NMR spectrum of polymer **G** at 60 °C.

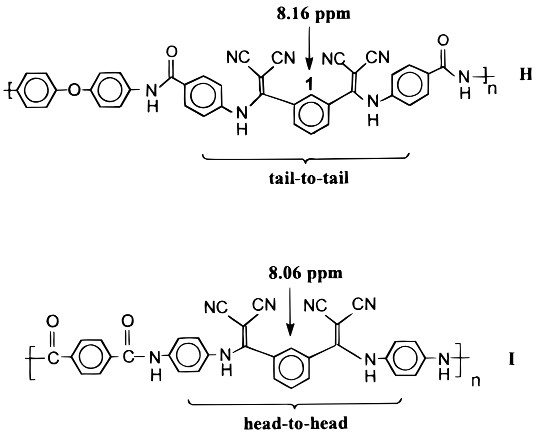


Figure 8. Repeat units of polymers **H** and **I** at 60 °C.

present as a singlet at 8.06 ppm and the copolymer structure is consistent with a head-to-head configuration. On the basis of this information, the peak between 8 and 8.25 ppm of copolymer **G** can be assigned accordingly, with 8.07 and 8.16 ppm as representative of head-to-head and tail-to-tail configurations, respectively. The peak at 8.11 ppm very likely represents contribution from head-to-tail configurations because it will be expected to lie between 8.07 and 8.16 ppm. Because the region between 8.0 and 8.25 ppm does not include peak areas from any other aromatic protons, the percent contribution from head-to-head and tail-to-tail configurations was calculated for copolymer **G** by taking the sum of the peak areas at 8.07 and 8.16 ppm over the total integral area of the region between 8.0 and 8.25 ppm. Proton deconvolution of this region aided in obtaining the relative integral areas to account for some of the overlapping observed.

Conclusions

The characterization of regularly alternating poly(amide−enaminonitriles) by ^{1}H and ^{13}C NMR spectroscopy was achieved by performing the experiments at 60−70 °C, using 2D NMR experiments (HMQC and TOSCY) to help with peak assignments, and by comparison to calculated values, spectral data of model compounds and previously reported data on poly(enaminonitriles). The structure of the copolymers made from an unsymmetrical amine, 4,4′-diaminobenzanilide, was found to be predominantly ordered where ^{1}H NMR data showed that 85% of the amino groups reacted via head-to-head/tail-to-tail selectivity.

References and Notes

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(4) The 1,3- or 1,4-bis(l-chloro-2,2-dicyanovinyl)benzene monomers (2.676 mmol) were added as solids to an equimolar solution of diamine and DABCO in 1.5% LiCl in DMAC over a period of about a half hour.

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(11) The NH resonances for poly(enaminonitriles) are typically found ~10.8−11.5 ppm while the amide NH for *N,N′*-bis(4-aminophenyl)terephthalamide is observed at 10.0 ppm. The latter shifts downfield only slightly (~0.2 ppm) when reacted with 1,3- or 1,4-bis(1-chloro-2,2-dicyanovinyl)benzene.

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