Revisions to the Microstructural Assignments of Poly(ethyl cyanoacrylate)

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ABSTRACT: The tacticity assignments from the literature for the ^{13}C-NMR signals of the side-chain methylene group of poly(ethyl cyanoacrylate) are reversed, and new assignments of the main-chain methylene group are proposed. The assignments were made possible by a combination of DEPT and HETCOR NMR experiments on samples of varying microstructure distributions. The polymer tends toward syndiotacticity, not isotacticity as previously reported. The distribution of stereoisomers fits well to a Bernoulian statistical model. The stereochemical assignments were corroborated by similar analyses of a model compound for two cyanoacrylate repeat units. © 1999 John Wiley & Sons, Inc. J Polym Sci A: Polym Chem 37: 2219–2224, 1999
Keywords: polycyanoacrylate; tacticity; microstructure; stereochemistry; NMR; DEPT; HETCOR; model compound; dimer

INTRODUCTION

As part of a program exploring the chemistry and applications of cyanoacrylate polymers, we had occasion to reexamine the ^{13}C-NMR assignments of the microstructure of poly(ethyl cyanoacrylate) (PECA, **1**).

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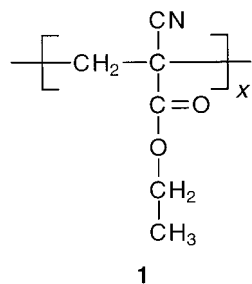
Previous workers[1,2] assigned the furthest downfield resonance (in acetone-d$_6$) of the side-chain methylene carbon atom of PECA to the *rr* triad. In addition, they reported that certain sam-

ples tended toward isotacticity. We employed the modern NMR techniques[3–5] of DEPT (Distortionless Enhancement Polarization Transfer) and ^{1}H-^{13}C HETCOR (Heteronuclear Correlation), which may not have been available to previous workers in this area, using two samples of rather different microstructural distributions. We have concluded that *the literature triad assignments must be reversed.*

EXPERIMENTAL

Ethyl cyanoacrylate was obtained from the Henkel Adhesives Corporation, and was used without further purification. Diethyl 2,3-dicyanoglutarate is a by-product from ethyl cyanoacrylate synthesis, and was obtained from Kodak. *t*-Butyl bromide (Aldrich) was dried over molecular sieves. Tetrahydrofuran (THF) was dried by distillation from calcium hydride under nitrogen. Ethanol was dried by distillation from magnesium under nitrogen. Methyl iodide, magnesium, and sodium were obtained from Aldrich.

Size Exclusion Chromatography (SEC) was obtained using three PLgel 10-mm mixed-bed col-

umns, calibrated with narrow MW distribution polystyrene standards. The eluent was dichloromethane/dichloroacetic acid (20/80%) containing 0.01 M tetrabutyl ammonium acetate.[6,7]

Sample A: Synthesis of Poly(ethyl cyanoacrylate) by Anionic Polymerization with *t*-Butyl Magnesium Bromide Initiator

The initiator was prepared by reacting 0.355 g (14.6 mmol) of magnesium with 2.00 g (14.6 mmol) of *t*-butyl bromide in 20 mL of anhydrous ether at reflux under nitrogen for 2 h. The resulting ethereal solution was cooled to room temperature, and used directly. To a stirred solution of 5.50 g (0.044 mol) of ethyl cyanoacrylate in 40 mL of dry tetrahydrofuran (THF) at −78°C under nitrogen was added 40 mL of a 0.73 M solution of *t*-butyl magnesium bromide in ether (above). The resulting mixture was stirred at −78°C for 15 min, and then gradually warmed to 25°C. The reaction mixture was poured into a solution of 600 mL of methanol containing 1 mL of concentrated hydrochloric acid. The precipitated polymer was filtered and dried *in vacuo*, producing 4.6 g (84%) of a white, fibrous solid. The product displayed a monomodal MW distribution by SEC: M_n = 36,400; M_w = 106,000.

Sample B: Synthesis of Poly(ethyl cyanoacrylate) by Zwitterionic Polymerization With Triethylamine Initiator

To a stirred solution of 5.00 g (0.040 mol) of ethyl cyanoacrylate in 40 mL of dry THF at −78°C under nitrogen was added 0.0040 g (0.040 mmol) of triethylamine. The resulting mixture was stirred at −78°C for 15 min, and then gradually warmed to 25°C overnight. The reaction mixture was poured into a solution of 600 mL of methanol containing 1 mL of concentrated hydrochloric acid. The precipitated polymer was filtered and dried *in vacuo*, producing 3.6 g (72%) of a white, fibrous solid. The product displayed a bimodal MW distribution: M_n = 18,300; M_w = 131,000 (overall). The lower MW fraction (approximately 40 wt %) was centered near 8000, and the higher MW fraction (approximately 60 wt %) was centered near 160,000.

Synthesis of Dimeric Model Compound 2

Sodium metal (0.39 g, 0.017 mol) was dissolved in 10 mL of dry ethanol under nitrogen, and a solution of diethyl 2,3-dicyanoglutarate (2.0 g, 0.008

mmol) in 8 mL ethanol was added with stirring. Methyl iodide (3.57 g, 0.025 mol) was added, the mixture was heated at reflux for 5 h, and then cooled. Most of the ethanol was removed at reduced pressure, and the residue was partitioned between 50 mL each of ether and water. The organic layer was separated, dried ($MgSO_4$), and concentrated to provide a tan oil. The oil was twice fractionally distilled at reduced pressure (b.p. 120–130°C/0.05 mm) to provide 0.60 g (28%) of a 56:44 mixture of **2r** and **2m**, respectively. ^{1}H-NMR (300 MHz, acetone-d_6) δ 1.3–1.4 (m, 6H), 1.68 (s, 3H, *r*), 1.76 (s, 3H, *m*), 2.52 (AB, J=14.7, 2H, *m*), 2.54 (s, 2H, *r*), 4.3–4.4 (m, 4H). ^{13}C-NMR (75 MHz, acetone-d_6) δ *r*-isomer: 14.01, 26.40, 42.55, 43.59, 63.78, 118.83, 169.05; *m*-isomer: 14.02, 25.42, 42.17, 42.97, 63.79, 119.33, 168.88.

NMR Experiment Information

The samples for NMR analyses were dissolved in acetone-d_6. Normal ^{13}C and DEPT experiments were carried out at 75.43 MHz on a Varian VXR-300S spectrometer. ^{1}H-^{13}C HETCOR (Heteronuclear Correlation) spectra were obtained at 30°C on a Varian Unity 500 spectrometer with a 5 mm PFG probe. The spectral width in the ^{1}H domain was 2849 Hz, and in the ^{13}C domain was 18752 Hz. A matrix of 1024 × 512 points with 32 transients per t_1 increment were acquired and zero filled to 2048 × 2048 points. Detection was in the ^{1}H domain.

RESULTS AND DISCUSSION

Polymer Synthesis

For this study, we prepared two samples by polymerizing ethyl cyanoacrylate monomer, the first initiated with *t*-butyl magnesium bromide (sample A) and the second initiated with triethylamine (sample B). Both polymerizations were carried out in dry tetrahydrofuran at −78°C, and the polymers were precipitated into excess acidified methanol, filtered, and dried in a vacuum oven.

Polymer Microstructure Studies by NMR

The first difficulty in assigning the microstructure of PECA lies in the overlapping resonances for the main-chain methylene and methine carbons. This complication can be removed using the DEPT pulse sequence, for which only carbons
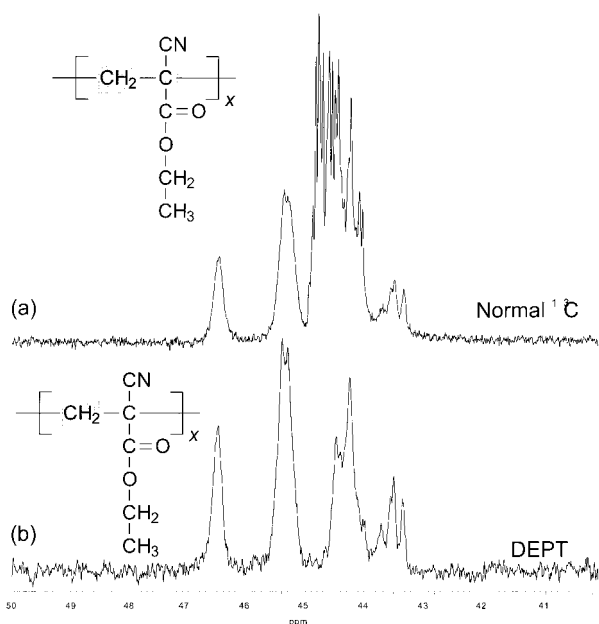
Figure 1. Normal ^{13}C and DEPT NMR of the main-chain methylene and methine region of PECA, sample A (synthesized using a *t*-butyl magnesium bromide initiator). The spectra were observed in acetone-d_6 at 75.43 MHz.

bearing hydrogens are observed, as illustrated for sample A in Figure 1.

The second difficulty lies in reconciling the relative intensities of the signals for the side-chain methylene (triad tacticity) and the main-chain methylene (tetrad tacticity), as illustrated in Figure 2 for sample B.

We attempted to make tetrad assignments to the main-chain methylene ^{13}C peaks with the help of a [1]H-^{13}C HETCOR experiment. In particular, the *rrr* and *mrm* tetrads are symmetrical about the main-chain methylene, and the attached protons exhibit a *singlet,* while the other four possibilities (*mmm*, *mmr*, *rmr*, and *rrm*) are expected to give rise to *two peaks* in the ^{1}H spectrum of their attached hydrogens. (Note that the observed proton linewidths are sufficiently broad to obscure [1]H-[1]H *J* couplings. Ordinarily, the less symmetrical methylenes should have displayed AB quartets.) As is clearly visible in Figure 3, the furthest upfield and downfield ^{13}C signals (i.e., ca. δ 43.5 and 46.5) are correlated with singlets in the ^{1}H spectrum; therefore, these peaks must be due to *rrr* or *mrm* tetrads.

It is impossible to reconcile the relative intensities of the ^{13}C signals for the side-chain methylene triads with those for the main-chain methylene tetrads using the literature triad assignments.[1,2] In particular, Bovey[8] teaches that the following relationships between triad and tetrad intensities must hold in all cases:
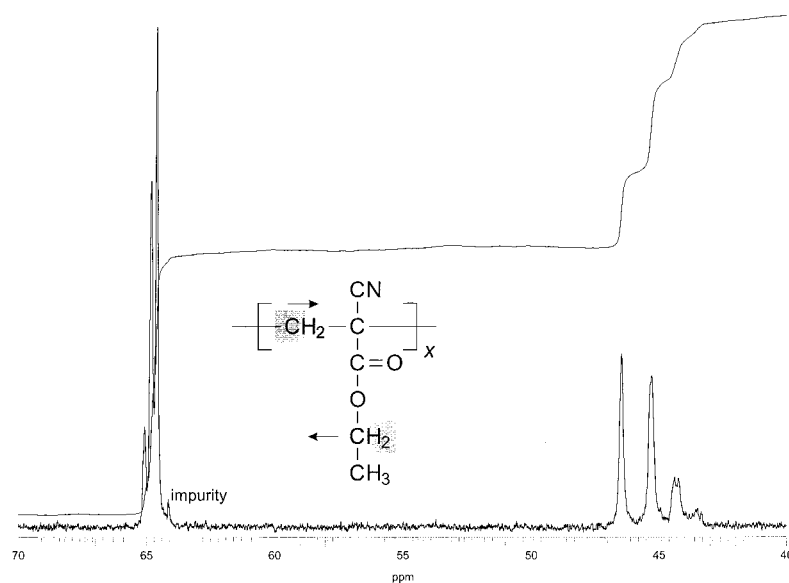

Figure 2. DEPT spectrum of PECA, sample B (synthesized using a triethylamine initiator). The spectrum was observed in acetone-d_6 at 75.43 MHz. Tacticity assignments for the main-chain methylene carbons follow from the HETCOR data shown in Figure 3.
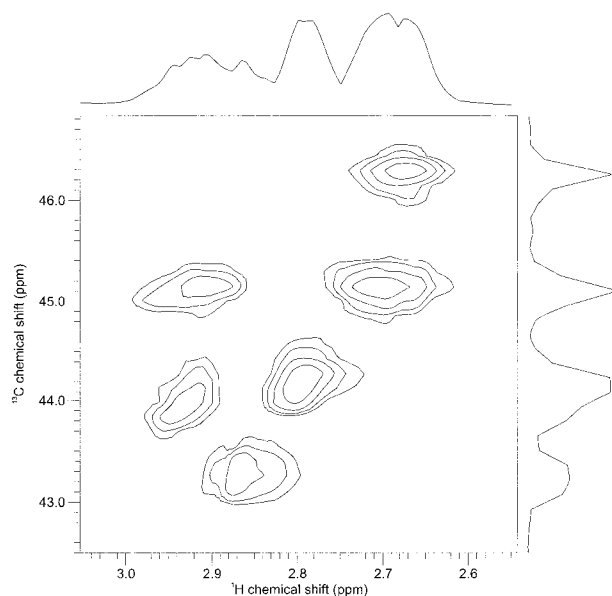
Figure 3. HETCOR of the main-chain methylene region for PECA, sample A (synthesized using a *t*-butyl magnesium bromide initiator). The spectra were observed in acetone-d_6 in the proton domain at 500 MHz. The vertical axis displays the ^{13}C chemical shift, and the horizontal axis displays the ^{1}H chemical shift of the attached hydrogen atoms. Projections of the 2D spectra in the ^{1}H and ^{13}C domains are shown above and to the left, respectively. Note that at this field strength, the geminal ^{1}H-^{1}H *J*-couplings are less than the observed proton linewidths, so that dissymmetric methylenes display two rather than four peaks in the ^{1}H domain.

$$rr = rrr + \tfrac{1}{2}\, mrr$$

$$mr = mrr + 2mrm$$

Neither of these necessary relationships can follow from the triad assignments from the literature, especially for sample B, as depicted in Figure 2. The peak at δ 46.5 is simply too large.

However, if one *reverses* the literature assignments for the side-chain methylene (i.e., assumes the furthest downfield ^{13}C signal is due to the *mm* triad, and the furthest upfield to the *rr* triad, instead of vice-versa), the tetrad assignments can be made in a completely consistent manner. The ^{13}C signal at δ 46.5 must then be due to *rrr*, and that at δ 43.5 due to *mrm*. The remaining main-chain methylene resonances can be tentatively assigned so that the intensities of all peaks visible in the DEPT spectra are consistent with Bernoulian statistics (Table I), assuming a probability of *meso* placement (P_m) of 0.50 for sample A (initiated with *t*-butyl magnesium bromide), and 0.30 for sample B (initiated with triethylamine). The revised triad and new tetrad assignments are shown in the DEPT spectrum of sample A in Figure 4.

We consider the assignments of the *rmr*, *rrm*, *mmm*, and *mmr* tetrads to be tentative because we do not have independent substantiating data for these particular cases. Nevertheless, the tetrad assignments shown in Figure 4 are the only ones that fit Bernoulian distributions (Table I), and are also consistent with the observed triad peak intensities for both samples.

Apparently, the chemical shift difference between the geminal methylene protons in the *rrm* stereoisomer is larger than that of the *mmr* stereoisomer (Fig. 3). One might have expected the opposite, because, structurally, the *rrm* tetrad

Table I. Bernoulian Statistics for the Tacticity of the Side-Chain and Methylene ^{13}C Signals for PECA

Tacticity Assignments[a]	^{13}C Chemical Shift[b]	Sample A $P_m = 0.50$[c] Predicted	Sample A Found[d]	Sample B $P_m = 0.30$[c] Predicted	Sample B Found[d]
Triad					
mm	δ 65.1	0.25	0.26	0.09	0.11
mr	δ 64.7	0.50	0.46	0.42	0.41
rr	δ 64.5	0.25	0.28	0.49	0.48
Tetrad					
rrr	δ 46.5	0.13	0.16	0.34	0.35
rmr + *rrm*	δ 45.4	0.38	0.35	0.44	0.41
mmm + *mmr*	δ 44.3	0.38	0.34	0.16	0.18
mrm	δ 43.5	0.13	0.14	0.06	0.06

[a] Assignments are from this work. The assignments of tetrads *rmr*, *rrm*, *mmm*, and *mmr* are tentative.
[b] In acetone-d_6.
[c] P_m indicates probability of a *meso* placement.
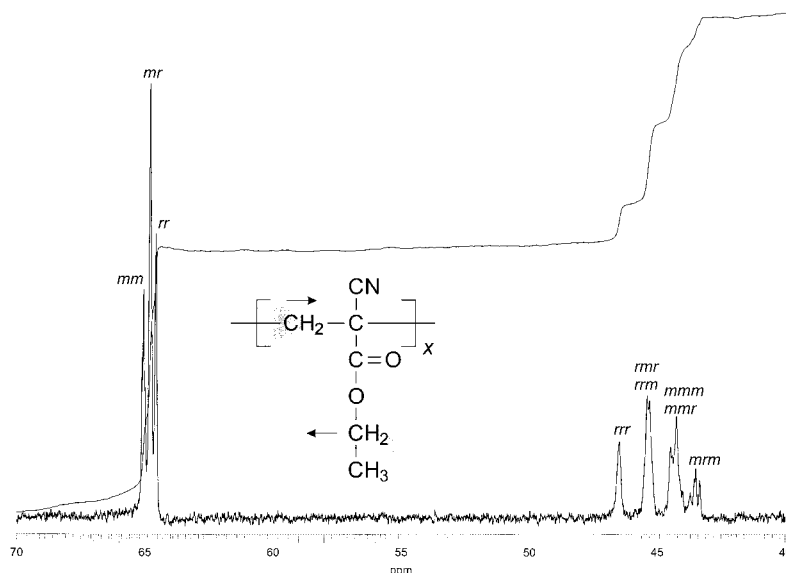[d] Data are taken from the DEPT spectra of Figures 2 and 4.

Figure 4. DEPT spectrum of PECA, sample A (synthesized using a *t*-butyl magnesium bromide initiator). The spectrum was observed in acetone-d_6 at 75.43 MHz. Tacticity assignments are from this work.

seems to be more symmetrical than the *mmr* tetrad from the point of view of the central methylene. Indeed, this expected behavior has been observed for the closely related polymer, polymethacrylonitrile.[9]
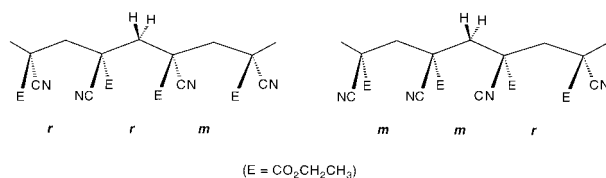

However, in the case of PECA, the presence of the highly polar and magnetically anisotropic cyano group presumably perturbs the chemical shifts of the methylene protons of one or both of these stereoisomers in the preferred local chain confirmation to give rise to the observed shifts.

The differences in tacticity between the two PECA samples may be attributable to the different counterions present during chain growth. Presumably, the counterion influences the chain conformation at the growing end, and may also affect the accessibility of incoming monomer. In addition, the syndiotactic content of sample B may have been enhanced by the relatively long time that the material was held in solution during synthesis. We have found that the distribution of stereoisomers in PECA equilibrates spontaneously in solution, tending toward syndiotactic

placement (according to the assignments made herein). This observation may be related to the changes in the molecular weight observed for solutions of poly(butyl cyanoacrylate) in the presence of added base, as reported by Ryan and McCann.[10] Details of our studies in this area will be reported in a forthcoming publication.

Model Compound Studies

To substantiate our assignments, we also synthesized a model compound **2** (which contains two repeat units of polymer **1**) by double alkylation of diethyl 2,3-dicyanoglutarate (**3**) with methyl iodide. Compound **2** was isolated as a 56:44 (*r:m*) mixture of diastereomers.
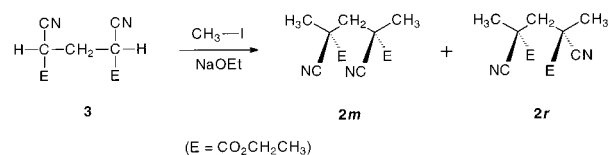
[1]H-^{13}C HETCOR analysis was used to make assignments of the carbon resonances of **2**, and the results corroborate the assignments for polymer **1** as proposed in this study. For example, the furthest downfield signal for the side-chain methylene of polymer **1** is assigned to the *mm* triad, and the furthest downfield peak for the same

carbon in the model compound **2** is due to the *m* diastereomer. Similarly, the furthest downfield main-chain methylene signal in the polymer **1** is assigned to the *rrr* tetrad, and the corresponding peak for the model compound **2** is due to the *r* diastereomer.

CONCLUSIONS

With these new assignments, it can be seen that poly(ethyl cyanoacrylate) initiated by an amine tends toward *syndiotacticity, not isotacticity,* as previously reported[1,2] (cf. Fig. 2). This conclusion is consistent with the recognized tendency of analogous polymethacrylates to adopt syndiotactic placements. The sample of poly(ethyl cyanoacrylate) made with *t*-butyl magnesium bromide initiator displays a nearly ideal, equal distribution of stereoisomers, in contrast to methyl methacrylate, which is reported to be polymerized by the same initiator (albeit in a nonpolar solvent, toluene) to produce highly isotactic PMMA.

We are currently examining stereochemical changes that occur when poly(ethyl cyanoacrylate) is held for periods of time in solution. A complete report will be published in due course.

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