Below a critical stoichiometric ratio p_c, samples are a collection of finite clusters which can be completely extracted ($G = 0$). Beyond p_c, samples present a giant cluster which cannot be extracted. The experimental results obtained with samples prepared at the two lower p values (see the table) lead us to locate the p_c value inside the following range: $0.5617 < p_c < 0.5632$. This p_c location is different from the $p_c = 0.5596$ determined by solubility measurements in a similar system.[1] This discrepancy can be explained by the fact that the material used did not come from the same synthesis run.

In the ϵ range investigated ($\epsilon \leq 3.8 \times 10^{-2}$), following the mean-field theory the gel fraction G should be a linear function of the reaction extent p, or approximatively linear (see eq 3). This is ruled out by Figure 1 which shows that the evolution of G as a function of p, on a linear scale, presents a strong downward curvature. In Figure 2, $G^{1/\beta}$ is plotted as a function of p where β is the exponent value deduced from the τ and γ values measured below the gel point ($\beta = 0.43 \pm 0.12$). The linear behavior in this representation (Figure 2) indicates that this β value is compatible with the present results but the p_c value determined in this manner $p_c = 0.5639$ is slightly out the p_c range evaluated from direct extraction measurements. This fact can be due to the difficulties encountered in the extraction of finite polymer clusters very near the gel point.

However, these results show clearly that the growth of polyurethane polymer clusters elaborated below and beyond the gel point is described by the percolation theory. But more experiments must be performed, beyond the gel point, in order to determine more precisely the exponent β and the law governing the decrease of the weight-average molecular weight.

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Communications to the Editor

Novel Nitrogen-Containing Heterocyclic Polymers Derived from the Alternating Ethylene–Carbon Monoxide Copolymer

We have recently described a mild, Pd(II)-catalyzed, procedure for the alternating copolymerization of ethylene and carbon monoxide (eq 1).[1] Because of the ease with

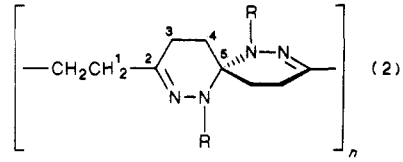
$$CH_2{=}CH_2 + CO \xrightarrow[25\ ^\circ C]{Pd(PPh_3)_n(MeCN)_{4-n}^{2+}} -(CH_2CH_2CO)_n- \quad (1)$$

which the carbonyl group can be chemically modified, polyketones such as the ethylene—carbon monoxide copolymer (E–CO copolymer) should be excellent precursors for other classes of functionalized polymers. Indeed, about two dozen functionalized polymers incorporating a variety of functional groups have been made starting with the previously reported random E–CO copolymer (C_2H_4:CO > 1).[2] As a precursor polymer, the alternating E–CO copolymer (C_2H_4:CO = 1) has two significant advantages over its random analogue (C_2H_4:CO > 1). First, since carbon monoxide does not homopolymerize, the alternating E–CO copolymer would provide the highest possible concentration of carbonyl groups in the polymer backbone. Second, the 1,4 arrangement of the carbonyl groups in the alternating E–CO copolymer makes additional functionalization procedures possible. Herein, we report the conversion of the alternating E–CO copolymer to two new classes of nitrogen-containing heterocyclic polymers through reactions based on the 1,4 arrangement of carbonyl groups in the backbone.

The addition of hydrazine to a MeOH suspension of the E–CO copolymer at 60 °C caused its complete dissolution to form a new polymer, **1**, in near quantitative yield. Following filtration to remove trace impurities, the polymer was isolated by the removal of the solvent. Reprecipitation from CH_2Cl_2–Et_2O yielded an off-white crystalline solid. An analogous reaction of methylhydrazine with the E–CO copolymer produced polymer **2** in near quantitative yield as a crystalline yellow-brown solid.

The structures of both polymers, **1** and **2**, were determined by spectroscopic methods and contained a unique spirofused group (1,2,7,8-tetraazaspiro[5.5]undecane) in the backbone (eq 2). The IR spectrum (Nujol) of polymer **1** exhibited $\bar{\nu}$(N–H) at 3250 cm^{-1}, $\bar{\nu}$(C=N) at 1630 cm^{-1}, and $\bar{\nu}$(C–N) at 1050 cm^{-1}. In its ^{1}H NMR spectrum (CD-

$$-(CH_2CH_2COCH_2CH_2COCH_2CH_2CO)_n- \xrightarrow[CH_3OH]{RNHNH_2}$$



(2)

polymer **1**, R = H; polymer **2**, R = CH_3

Cl_3), three resonances were observed at 2.36, 2.25, and 1.77 ppm with integral ratios of 1:1:1, and these were assigned to the three $-CH_2-$ groups present. The highest field signal was ascribed to the hydrogens on C-4. In addition, the spectrum contained a broad resonance at 6.3–5.8 ppm due to the –NH group. A tiny triplet at 1.06 ppm (J = 7.6 Hz) due to the terminal $-CH_3$ groups of the polymer was also observed. The ^{1}H-coupled ^{13}C NMR spectrum ($CDCl_3$) showed three triplets at 34.1 ppm (J = 129.9 Hz), 28.1 ppm (J = 131.4 Hz), and 22.1 ppm (J = 125.5 Hz) due to the three $-CH_2-$ groups. In addition, singlets were observed at 148.1 and 59.8 ppm and were ascribed to C-2 and C-5, respectively.

Polymer **2** showed NMR spectral features analogous to **1** except that the broad resonance at 6.3–5.8 ppm was replaced by a singlet at 2.71 ppm in the ^{1}H NMR spectrum ($CDCl_3$), and a quartet at 36.7 ppm (J = 135.7 Hz) was observed in the ^{1}H-coupled ^{13}C NMR spectrum ($CDCl_3$). These additional resonances were due to the presence of $N-CH_3$ group in polymer **2**. In neither polymer was there any evidence for the presence of unreacted carbonyl groups.

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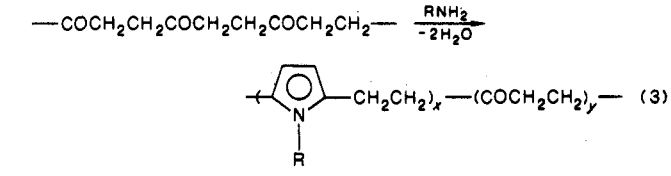
Identical spirofused bicyclic ring systems were also formed by the reaction of hydrazine and methylhydrazine with the model trione 3,6,9-undecatrione.[3] The close analogy between the NMR spectral features of the products derived from the trione and those from the E–CO copolymer further confirmed the structures of polymers **1** and **2**.

Polymers **1** and **2** exhibited markedly enhanced solubility when compared to the starting E–CO copolymer, which is insoluble in most common solvents. Both **1** and **2** were soluble in a range of organic solvents, with the solubility of **1** being higher in protic solvents such as MeOH.

The E–CO copolymer was also found to react with primary amines to form poly(ethylenepyrrole) derivatives in accordance with eq 3.[4] The reaction appears to be quite



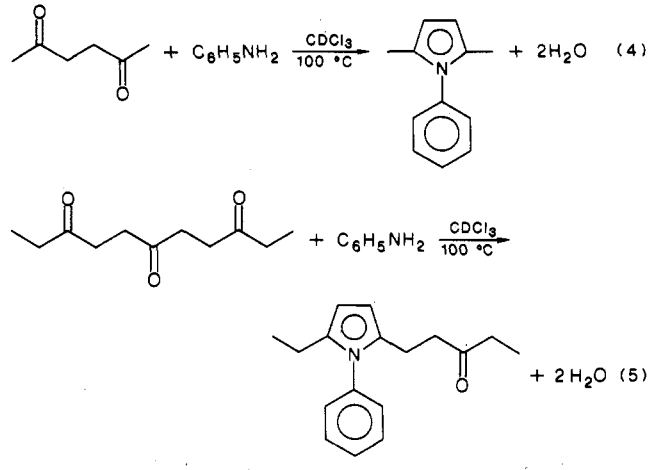
(3)

general and is tolerant of a wide variety of other functionalities on the primary amine such as $—NR_2$, —OH, and $—CH=CH_2$. The reactions were usually carried out at 100–150 °C under an inert atmosphere. With amines that were liquids within that temperature range, no solvent was used. In a typical reaction, 2 g of the E–CO copolymer was added to 30 mL of aniline, and the reaction mixture was stirred at 130 °C for 1 day. At the end of this period, a viscous solution was obtained. This was filtered, and then a yellow polymer was precipitated by the additon of Et_2O and pentane. Following reprecipitation from CH_2Cl_2–pentane, a >90% yield of polymer **3** (R = C_6H_5) was obtained.

Reaction 3 appears to be dominated by steric effects rather than the relative basicity of the amines employed. For example, similar rates were observed with all the amines of the type RCH_2NH_2. Slower rates were observed with RNH_2 (R = phenyl, cyclohexyl). Furthermore, the rates for the latter two amines were similar although $C_6H_{11}NH_2$ is a significantly stronger base than $C_6H_5NH_2$. Finally, no reaction was observed with the bulky *t*-$BuNH_2$.

The structures of the poly(ethylenepyrrole) derivatives were established by spectroscopic methods, especially ^1H and ^{13}C NMR spectroscopy. For example, the ^1H NMR spectrum ($CDCl_3$) of polymer **3** consisted of three major resonances at 7.3–6.8, 5.8–5.6, and 2.5–2.3 ppm in the intensity ratio of 200:75:180, and these were assigned to the hydrogens of the phenyl ring, the pyrrole methine groups, and the methylene groups, respectively. In addition, there was a small triplet due to the terminal methyl groups of the polymer. The ratio of the number of carbonyl groups reacted to the total number of carbonyl groups originally present, $2x/(2x + y)$ (see eq 3), was determined to be 0.92 from the intensity ratio of the methine and the methylene groups. The ^1H-coupled ^{13}C NMR spectrum ($CDCl_3$) of this polymer exhibited a singlet and three doublets at 138.24, 128.99, 128.32, and 127.74, ppm, respectively, due to the phenyl carbons and singlet and a doublet at 133.40 and 104.48 ppm, respectively, due to the carbons of the pyrrole unit. In addition, there were three triplets at 41.64, 26.79, and 20.85 ppm in the intensity ratio of ~1:6:1. The first and the last of these resonances were due to the methylene groups between a pyrrole unit and an unreacted carbonyl group, while the peak at 26.79 ppm was due to the methylene groups between two pyrrole units. The intensity ratios indicated the value of $2x/(2x + y)$ to be 0.88.

The above structural assignments were confirmed by comparison with the NMR spectral data of the products formed by the reaction of aniline with the model compounds 2,5-hexadione (eq 4), and 3,6,9-undecatrione (eq 5). It is interesting to note that, as shown by eq 5, even



an excess of aniline did not appreciably react with a *single* carbonyl group to form a Schiff base.[5] Clearly, therefore, the irreversible formation of the aromatic pyrrole unit was the driving force in the reaction of amines with the E–CO copolymer.

Unlike the parent E–CO copolymer, the poly(ethylenepyrrole) derivatives were thermoplastic materials (T_g = 70 °C for **3**) which exhibited good solubility in common organic solvents. For example, **3** was readily soluble in CH_2Cl_2 and $CHCl_3$.

A curious point concerning both classes of polymers is the unusually small number of unreacted carbonyl groups that remain after the cyclization step. For example, in the reaction with hydrazines where three adjacent carbonyl groups are involved in the cyclization step, ~100% of the carbonyl groups was found to have reacted. In the reaction with amines, which involves two carbonyl groups at a time, the numbers of reacted carbonyl groups were as follows: R = C_6H_5–, 92%; *p*-ClC_6H_4–, 99%; *p*-MeC_6H_4–, 95%; *n*-butyl, 90%. Given the observed irreversibility of the cyclization step, these values are clearly higher than what would be expected if the incoming reagent could attack any part of the E–CO copolymer chain at random leaving behind isolated, unreacted, single carbonyl groups. In view of the high insolubility of the E–CO copolymer in the reaction medium, the above values indicate that the cyclization reactions started from the end of an E–CO copolymer chain and proceeded toward the middle as the derivatized polymer segment dissolved.

Finally, the solubility of **3** allowed us to determine, for the first time, the molecular weight of the starting E–CO copolymer. With GPC techniques and polystyrene standards, a molecular weight of approximately 9000 and a dispersity ($\bar{M}_w/\bar{M}_n$) of 1.8 were obtained for **3**. This translates to $n \sim 100$ for the precursor $-(CH_2CH_2CO)_n-$.

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(2) (a) Reference 1a. (b) Sen, A. *Adv. Polym. Sci.* **1986**, *73/74*, 125, and references therein.
(3) (a) In a previous publication, a different structure was reported for the product of the reaction between the trione and hydrazine; see: Stetter, H.; Landscheidt, A. *J. Heterocycl. Chem.* **1979**, *16*, 839. (b) Spectral data for product derived from hydrazine. ^{1}H NMR ($CDCl_3$) (ppm): 1.08 (t, J = 7.6 Hz, 6 H), 1.75–1.84 (m, 4 H), 2.17 (q, J = 7.6 Hz, 4 H), 2.18–2.25 (m, 4 H), 5.70 (s, br, 2 H). ^{13}C NMR (H coupled) ($CDCl_3$) (ppm): 11.0 (tq, J = 126.7, 4.7 Hz), 22.2 (t, J = 127.1 Hz), 28.4 (t, J = 129.6 Hz), 30.2 (qt, J = 126.2, 4.2 Hz), 60.1 (s), 150.5 (s). Ir (Nujol) (cm^{-1}): 1635 (C=N), 3350 (N–H). Mass spectrometry: 208 (M^+). (c) Spectral data for product derived from methylhydrazine. ^{1}H NMR ($CDCl_3$) (ppm): 1.01 (t, J = 7.6 Hz, 6 H), 1.62 (td, J = 12.9, 4.8 Hz, 2 H), 1.83 (td, J = 13.0, 8.8 Hz, 2 H), 2.11 (q, J = 7.6 Hz, 4 H), 2.13 (m, 4 H), 2.71 (s, 6 H). ^{13}C NMR (H coupled) ($CDCl_3$) (ppm): 11.5 (tq, J = 126.7, 4.7 Hz), 19.1 (mt, J = 130.5 Hz), 23.0 (mt, J = 127.8 Hz), 30.3 (qt, J = 126.5, 4.3 Hz), 36.8 (q, J = 135.7 Hz), 68.8 (s), 147.4 (s).
(4) Similar poly(ethylenepyrrole) polymers have been patented by Shell; see: Kiovsky, T. E.; Kromer, R. C. U.S. Patent 3979374, 1976. However, these have significantly fewer pyrrole units in the chain. The value of $2x/(2x + y)$ (see text) varied between 0.33 and 0.04 compared to ≥0.90 for the polymers that we report.
(5) This is true under conditions where the H_2O generated in the reaction is not removed, as is the case for the reactions described.

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Comments on the α to β Transition in Poly(butylene terephthalate)

A recent paper published by Tonelli et al.[1] using ^{13}C solid-state NMR to study the crystalline phase transition in poly(butylene terephthalate) (PBT) concluded that there are no chemical shift differences among the methylene carbons. From this experimental observation, it was concluded that the tetramethylene segment does not undergo any changes during the transition. This is contrary to the NMR data of Perry and Koenig[2] as well as to numerous other papers using infrared and X-ray.

PBT is known to undergo a reversible crystalline phase transition when uniaxially drawn. The phase change has been successfully followed by IR and X-ray measurements. A number of general conclusions have been obtained. The β phase has a larger unit cell that is evidenced by a lower density. This occurs as a result of the lengthening of the *c*-axis repeat distance.

The IR data conclusively show that the greatest changes occur in the methylene region of the spectra with the appearance of bands due to the β phase and the disappearance of those due to the α phase. The tetramethylene segment is in an extended configuration in the β phase and a crumpled configuration in the α phase. Intermolecular and intramolecular energy calculations on the β phase indicate that it is indeed a higher energy conformation.

Solid-state NMR is a useful technique for studying conformational changes as evidenced by the γ-gauche effect observed in polymers. However, a recent paper by Ando et al.[3] indicates that the trans and gauche conformations of the methylene carbons in poly(oxymethylene) have a nonlinear relationship with respect to the dihedral angle so that the chemical shift of two carbons in different conformational states may appear to be the same.

Past X-ray patterns indicate that there are significant differences between the two phases, most easily seen on the first and second layer lines (Figure 1). The X-ray patterns published by Tonelli et al. for the two phases both appear to be identical with the α-phase pattern of Figure 1 and not the β phase, also shown in Figure 1. It is also quite possible that some relaxation occurs at the elevated temperatures during the NMR measurements since the energy diffeences between the phases are quite small.

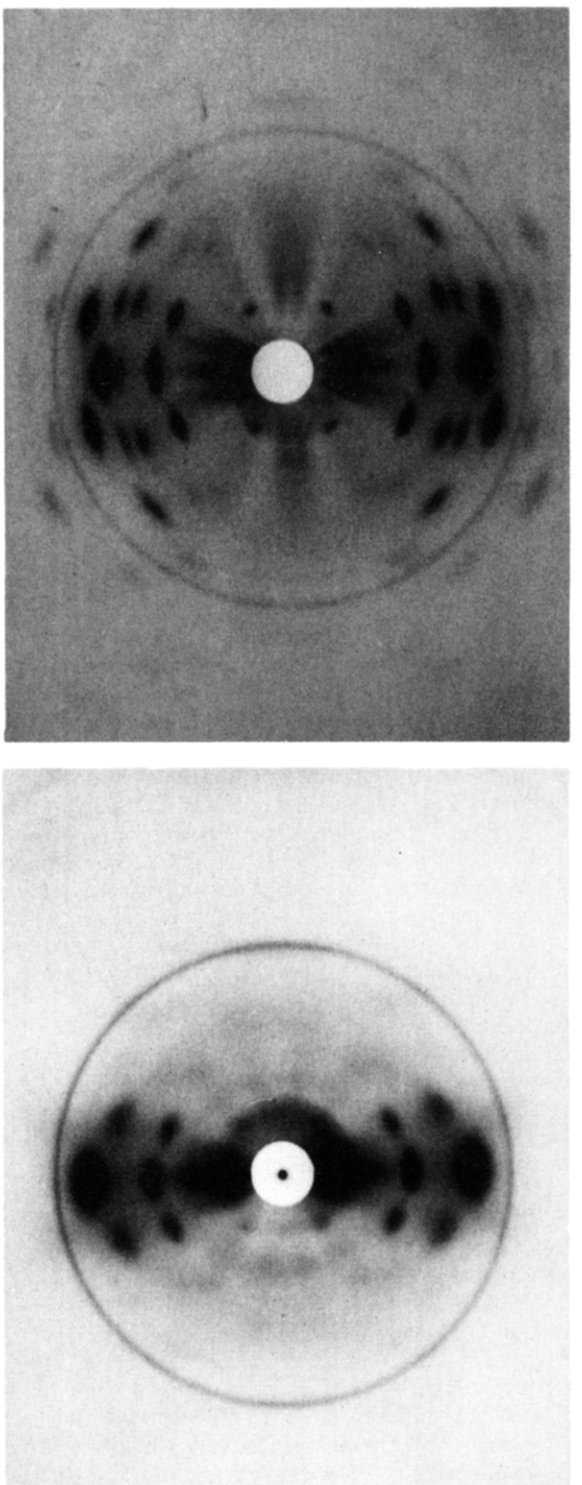

Figure 1. Wide-angle X-ray patterns of PBT in the (top) α phase and (bottom) β phase.

Considering the past IR and X-ray data and the similarities of the two X-ray patterns of Tonelli et al., we believe that one cannot conclude that there is no change in the tetramethylene segment of PBT when uniaxially drawn solely on the basis of the solid-state NMR measurements. An IR spectrum of the drawn sample before

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