Dipole Moments and Conformational Analysis of Copolymers of Ethylene and Carbon Monoxide

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ABSTRACT: Dipole moments have been determined of two semialternating ethylene–carbon monoxide copolymers with carbonyl contents of 40.3% and 42.6%, as well as of the low molecular weight model compounds 3-pentanone and 2,5-hexanedione. A rotational isomeric state scheme has been developed for copolymers of ethylene and carbon monoxide. The predictions of the model are in good agreement with the data from dipole moment measurements.

Introduction

Copolymers of ethylene and carbon monoxide have been known since Brubaker and co-workers first prepared them nearly 30 years ago in a free radical copolymerization reaction.[1,2] Nearly at the same time, Reppe copolymerized the two gases in water as solvent by means of a nickel(II) catalyst but only obtained oligomers; these products, however, displayed exclusively alternating ethylene–carbon monoxide sequences.[3] Later, a series of catalysts were found to produce high molecular weight copolymers, most of them containing palladium or nickel coordination complexes (see, for instance, ref 4–6). In contrast to the copolymers prepared through a free radical mechanism, the ones obtained by means of a metal catalyst usually show a highly alternating structure independent of the composition of the monomer mixture. The highly alternating copolymers are characterized by high crystallinity, high melting point, and very low solubility in most of the common solvents. They offer ample possibility for chemical modification[2,7] and are photodegradable under some conditions.[8–10] Yet, no full characterization of the alternating copolymer has appeared in the literature, probably due to its insolubility in most of the common solvents.

The insolubility of the alternating copolymer is not fully understood. In part it is certainly due to a comparatively high lattice energy in the crystallites as is indicated by the high melting point. But in principal it might also be due partly to a certain rigidity of the chain in solution. It is known from studies of the solid state[11–13] that the copolymer crystallizes in the planar zigzag conformation. But so far nothing is known about the conformational characteristics of ethylene–carbon monoxide copolymers in solution or in the amorphous state.

We report here the dipole moments of two low molecular weight semialternating[14] ethylene–carbon monoxide copolymer samples, determined by measuring the dielectric constant (relative permittivity[15]) of dilute solutions in a nonpolar solvent. Furthermore, the dipole moment of 2,5-hexandione, a model compound, was determined and is compared with that of 3-pentanone. Results are interpreted according to a rotational isomeric state scheme, developed for copolymers of ethylene and carbon monoxide.

Experimental Section

Ethylene and carbon monoxide were copolymerized in various runs by using a rhodium-containing catalyst.[16] The resulting copolymer samples had a number-average molecular weight of typically 3000 as determined by cryoscopy in camphor. They were mixed together and fractionated by boiling solvent extraction[17] under nitrogen by using successively cyclohexane, acetone, ethyl methyl ketone, diethyl ketone, isobutyl methyl ketone, diisopropyl ketone, and dipropyl ketone. For dipole moment measurements, the fractions soluble in boiling acetone and boiling dipropyl ketone were chosen. They were characterized by 300-MHz ^{1}H NMR in $CDCl_3$ at 25 °C, elementary analysis, viscosimetry in $CHCl_3$ at 25 °C, and DTA.

The alternating ethylene–carbon monoxide copolymers mentioned in the text were synthesized by using palladium[5] or nickel[6] catalysts, and hydrogen was added in order to control the molecular weights of the products.[18] The copolymer samples were purified according to a new method[19] and showed intrinsic viscosities in the range 0.4–5.7 dL/g measured in *o*-chlorophenol at 25 °C and DTA melting points between 252 and 255 °C.

3-Pentanone and 2,5-hexanedione were commercial products purified by fractional distillation over 3-Å molecular sieves. Dioxane was distilled over sodium prior to use.

The mean-square dipole moments per keto group were evaluated according to a simplified form of the Guggenheim–Smith equation,[20,21] which neglects the difference in atomic polarization between solute and displaced solvent, since its contribution is generally considered to be low:

$$\frac{\langle\mu^2\rangle}{n_k} = \frac{27kTM}{4\pi N_A d_1}\left[\frac{d\epsilon_r/dw}{(\epsilon_{r,1}+2)^2} - \frac{2n_1(dn/dw)}{(n_1^2+2)^2}\right] \quad (1)$$

Here d_1 is the density, $\epsilon_{r,1}$ the dielectric constant, and n_1 the refractive index of the solvent, N_A is Avogadro's number, k is Boltzmann's constant, T is the temperature, M is the average molar mass per keto group of the measured compound, w is its weight fraction, and n_k is the average number of keto groups per molecule. For the low molecular weight compounds the equation was suitably modified; M was taken to be the molar mass of the compound and n_k was set to unity.

In order to obtain values for the dielectric constant, ϵ_r, capacitances of dilute solutions were measured with a General Radio Model 1621 capacitance bridge assembly at a frequency of 10 kHz. The capacitance cell was constructed with concentric cylindrical stainless steel electrodes, separated by PTFE spacers. The cell volume was about 4.2 mL and the vacuum capacitance was 9.178 pF. The contribution of the spacers to the measured capacitance was evaluated by calibration with dioxane. Temperature control was achieved by immersing the cell into a water bath, which was held constant at 60.0 ∓ 0.1 °C. The experimental setup was tested by measuring the dipole moment of chlorobenzene.

Refractive index increments dn/dw were measured at a wavelength of 546 nm with a Brice-Phoenix differential refractometer which had been equipped with a heating device for the cuvettes.

For dioxane at 60 °C the following values were used: d_1, 0.988 49 g/cm^3;[22] $\epsilon_{r,1}$, 2.1495;[23] n_1, 1.405 13.[22]

Results and Discussion

Synthesis and Chain Structure. The proton NMR spectrum of the acetone soluble fraction is given in Figure 1; the one of the dipropyl ketone soluble fraction shows no significant difference. The peak assignments have been made according to Wu et al.[24] and are listed in Table I.

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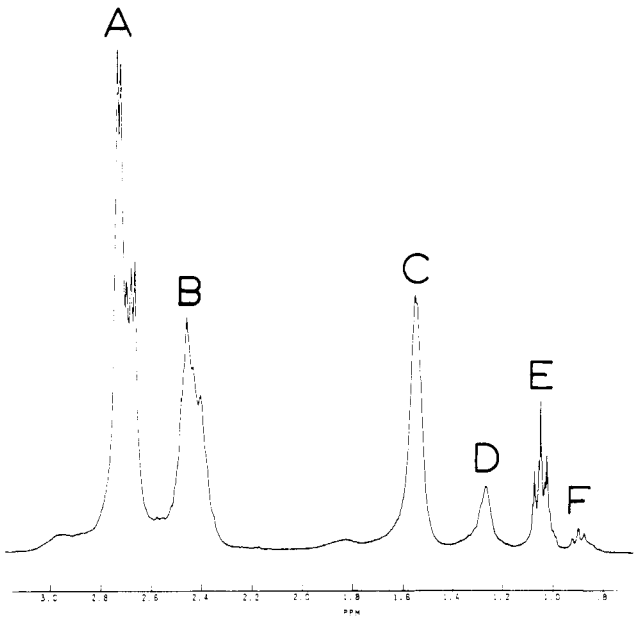

Figure 1. ^{1}H NMR spectrum of the acetone-soluble fraction (in $CDCl_3$, 25 °C, chemical shift in reference to TMS).

Table I
Relative Signal Intensities of ^{1}H NMR Peaks of the Ethylene–Carbon Monoxide Copolymer Samples Used for the Dipole Moment Measurements

signal	chem shift, ppm	rel signal intens[a] asf	dsf	assignment
A	2.70	1.00	1.00	$COCH_2CH_2CO$
B	2.43	0.58	0.41	$COCH_2CH_2CH_2CH_2CO$
C	1.55	0.49	0.36	$COCH_2CH_2CH_2CH_2CO$
D	1.27	0.13	0.07	$COCH_2CH_2(CH_2)_xCH_2CH_2CO$
E	1.05	0.15	0.06	$COCH_2CH_3$
F	0.90	0.04	0.02	$COCH_2CH_2CH_2CH_3$

[a] asf, acetone soluble fraction; dsf, dipropyl ketone soluble fraction.

According to these spectra, the structure of the ethylene–carbon monoxide copolymer obtained is semialternating[14] and alkyl moieties with an even number of carbon atoms are the only end groups observed.

The detailed mechanism of the copolymerization reaction used for synthesis of the samples mentioned above is not known. Lacking a more appropriate model, the following Markov scheme was applied to generate structures that agree with the NMR spectra:

$$q_{CO} = P_{COCO}/P_{COEt} = 0 \qquad q_{Et} = \frac{P_{EtEtEt}}{P_{EtEtCO}} \qquad (2)$$
$$q'_{Et} = P_{COEtEt}/P_{COEtCO}$$

where P_{ijk} is the conditional probability of finding monomeric unit k in the chain following the monomeric units i and j and P_{ij} the corresponding conditional probability for finding unit j following unit i. The fitted values of q_{Et} and q'_{Et} differ roughly by a factor of 2; values are listed in Table II.

NMR end-group analysis allows the estimation of M_n of the polymer chains. Under the assumption that no end groups are present other than the ones seen in signal E and F, M_n can be obtained from integration over the different peak areas as (see Figure 1 and Table I)

$$M_n = 28\frac{2A + 2B + C + D + \frac{2}{3}(E + F)}{\frac{2}{3}(E + F)} + 2 \qquad (3)$$

Table II
Markov Probability Scheme for the Generation of Chains Having Structures Which Yield the Same ^{1}H NMR Spectra as the Samples Used for Dipole Moment Measurements

	probability	value[a] asf	dsf
	symbol		
"chain start"[b]			
HEt → HEtEt	P_{Et}^s	same as for P_{EtEtEt}	
HEt → HEtCO	P_{CO}^s	same as for P_{EtEtCO}	
"chain growth"[b]			
CO → COCO		0	0
CO → COEt		1	1
	q_{CO}	0	0
EtEt → EtEtEt	P_{EtEtEt}	0.16	0.14
EtEt → EtEtCO	P_{EtEtCO}	0.78	0.82
	q_{Et}	0.21	0.17
COEt → COEtEt	P_{COEtEt}	0.33	0.26
COEt → COEtCO	P_{COEtCO}	0.61	0.70
	q'_{Et}	0.54	0.37
"chain termination"[b]			
Et → EtH	P_{Et}^t	0.061	0.0365
CO → COH		0	0

[a] asf, acetone soluble fraction; dsf, dipropyl ketone, soluble fraction. [b] Et = $-CH_2-CH_2-$.

Table III
Results of the Characterization of the Ethylene–Carbon Monoxide Copolymer Samples

sample[a]	^{1}H NMR M_n, g/mol	% CO	anal., % CO	visc[b] [η], dL/g	DTA T_m, °C
asf	880	40.3	43.5	0.106	101
dsf	1730	42.6	44.3	0.143	141

[a] See footnote to Table II. [b] At 25 °C in *o*-chlorophenol.

The resulting molecular weights for the two samples are listed in Table III together with the results of further characterizations. It is noteworthy, that the carbon monoxide contents obtained from elemental analysis and NMR spectra differ significantly. We feel that the results of elemental analysis are more reliable and precise, since the NMR spectra show small bands at ≈1.85 and 2.95 ppm that could not be identified (see Figure 1). They could easily introduce an error of the order of the deviations observed between the results of the two methods. However, for reason of internal consistency, we chose the monomer sequences deduced from the analysis of NMR spectra when the structure of the copolymers was required for computation.

A Rough Estimate of Chain Dimensions of Alternating Copolymers. In addition to the polymers described here, highly alternating copolymers of different molecular weights have also been prepared using palladium[5] and nickel[6] compounds as catalyst precursors. Because of the insolubility of these copolymers in nonpolar solvents, their mean-square dipole moment ratios could not be determined. However, intrinsic viscosity and osmometry measurements have been carried out in *o*-chlorophenol at 25 °C and it was possible, on the basis of these results, to obtain a rough estimate of the characteristic ratio of the unperturbed mean-square end-to-end distance;[25] $C_\infty = \lim_{n\to\infty} \langle r^2\rangle_0/nl^2$ is ca. 8.5 ∓ 1.5 at 25 °C. Because of the uncertainty concerning molecular weight distribution of the samples used, it was not possible to determine this value more accurately.[26]

Dipole Moments. Refractive index and dielectric constant increments had been measured for copolymer solutions in the concentration range of ≈1 to ≈6 mg/g in dioxane at 60 °C. In all cases examined the dependence

Table IV
Results of the Dipole Moment Measurements in Dioxane at 60 °C

compound	M	$d\epsilon/dw^a$	dn/dw^a	μ,[a] D
Low Molecular Weight Compounds[c]				
3-pentanone	86.14	9.02 ∓ 0.38	−0.0391 ∓ 0.0001	2.75 ∓ 0.06
2,5-hexanedione	114.15	8.46 ∓ 0.19	+0.0065 ∓ 0.00003	3.05 ∓ 0.03
Ethylene–Carbon Monoxide Copolymers				
asf[d]	69.50[b]	5.20 ∓ 0.30	+0.088 ∓ 0.001	0.43 ∓ 0.03
dsf[d]	65.70[b]	5.29 ∓ 0.24	+0.088 ∓ 0.001	0.42 ∓ 0.03

[a] Value plus/minus standard deviation. [b] Per carbonyl group. [c] $D_\infty = \langle\mu^2\rangle/n_k\langle\mu^2\rangle_{co}$. [d] See footnote to Table II.

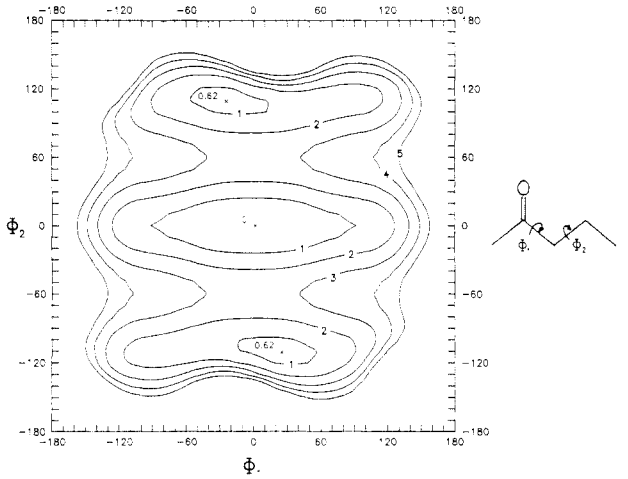

Figure 2. Contour map of the potential energy of 2-pentanone as a function of the two torsion angles Φ_1 and Φ_2. Torsion angles are zero in the conformation depicted. Energy contours are drawn at 1, 2, 3, 4, and 5 kcal/mol relative to the absolute minimum at $\Phi_1 = \Phi_2 = 0$.

on concentration was found to be linear, and a linear least-square fit was used to analyze the data. Results and standard deviations are given in Table IV.

The result of the dipole moment measurement for 3-pentanone is in agreement with literature values.[27]

Conformational Energies. Conformational potential energies for 2-pentanone, 3-pentanone, and 2,5-hexanedione were estimated with a classical force field. Bond length and bond angles were kept fixed at values used earlier.[28] Methyl and methylene groups were treated as spherical "quasi"-atoms. The potential energy of any given conformation was assumed to be the sum of "van der Waals interactions" of all pairs of nonbonded atoms, intrinsic rotational potentials of all single bonds about which rotation can occur, and Coulombic interactions between all charged atoms. Details of this potential function as well as information on the treatment of solvent interaction are given in ref 28. Conformational energies were calculated at 10° intervals for all torsion angles and the data are represented by contour maps. These maps for 2-pentanone and 3-pentanone are given in Figures 2 and 3. In the case of 2,5-hexanedione contour maps have been drawn keeping the third rotational angle fixed at selected values; the one for $\Phi_3 = 0°$ is given in Figure 4. The maps of all three compounds show that rotation about all CH_2–CH_2 bonds can be described with the classical three states "trans", t, "gauche plus", g^+, and "gauche minus", g^-. Rotation about the CO–CH_2 bond is much less restricted; only one extremely wide energy minimum around the trans conformation is observed, the only rotational barrier being at 180°.

The differences in the maps presented in Figures 2 and 3 and those given earlier are indicative of an inconsistency in the earlier work,[28] where methylene groups were represented sometimes as spherical quasi-atoms and sometimes with explicit hydrogen atoms.

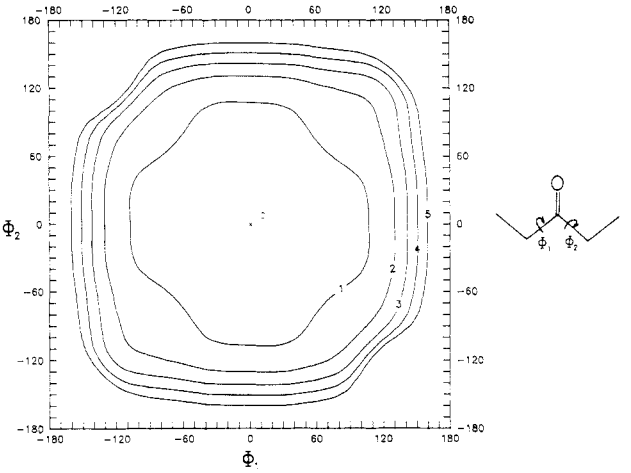

Figure 3. Contour map of the potential energy of 3-pentanone as a function of the two torsion angles Φ_1 and Φ_2. Torsion angles are zero in the conformation depicted. Energy contours are drawn at 1, 2, 3, 4, and 5 kcal/mol relative to the absolute minimum at $\Phi_1 = \Phi_2 = 0$.

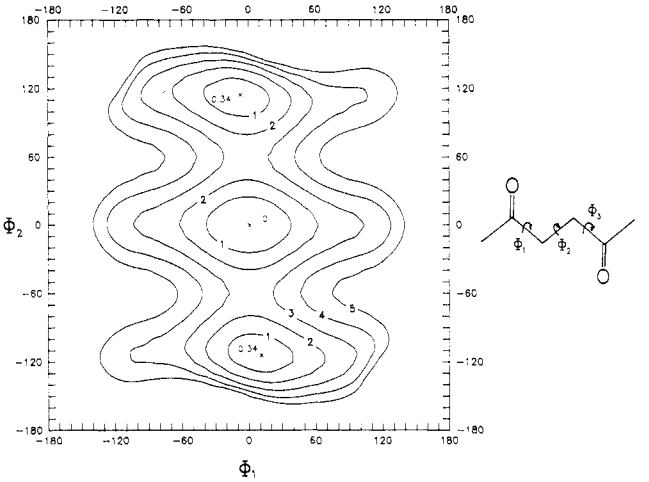

Figure 4. Contour map of the potential energy of 2,5-hexanedione as a function of the two torsion angles Φ_1 and Φ_2; Φ_3 was kept fixed at 0. Torsion angles are zero in the conformation depicted. Energy contours are drawn at 1, 2, 3, 4, and 5 kcal/mol relative to the absolute minimum at $\Phi_1 = \Phi_2 = \Phi_3 = 0$.

A Rotational Isomeric State Model. A rotational isomeric state (RIS) model for ethylene–carbon monoxide copolymers must take account of the fact that in the case of CO–C_2H_4–CO sections two carbonyl groups occur in the 1,4-position. Usually, only second-order interactions must be considered in the RIS models. The carbonyl–carbonyl interaction is of third order, but inspection of models indicates that it cannot be neglected. Detailed calculations reveal that the differences in the interaction energies attributable to such third-order interactions are of about 1 kcal/mol; therefore, they must be considered. It is, however, possible to account for this interaction by the introduction of a pseudo-second-order parameter (see below), which has the consequence that bonds within a CO–C_2H_4–CO section have to be treated differently from chemically identical bonds in CO–$(C_2H_4)_x$–CO sections, where $x > 1$. Consequently, seven different types of statistical weight matrices are needed for an RIS scheme of ethylene–carbon monoxide copolymers (see Figure 5). The statistical weight parameters for matrices A, B, and C have to be evaluated through calculations on 2,5-hexanedione, while those for matrices a, b, and c can be obtained through calculations on 2-pentanone and 3-pentanone, respectively.

Table V
Integration Results for the Eight Distinguishable Rotamers of 2-Pentanone

rotamer Φ_1	rotamer Φ_2	multiplicity	partition fcn[a,b]	av energy,[a] kcal/mol	$\langle\Phi_1\rangle$	$\langle\Phi_2\rangle$
t^-	t	2	0.752	0.21	−38	0
t^0	t	1	1.	0.	0	0
t^-	g^+	2	0.327	0.69	−38	108
t^0	g^+	2	0.287	0.72	−2	102
t^+	g^+	2	0.170	1.15	39	100
g^+	t	2	0.486	1.02	88	0
g^+	g^+	2	0.193	1.60	90	107
g^+	g^-	2	0.141	1.55	78	−106

[a] Partition functions and energies are given relative to the t^0t-conformation. [b] Integral of $\exp(-E/kT)$ over the conformational domain of the rotamer.

Table VI
Integration Results for the Nine Distinguishable Rotamers of 3-Pentanone

rotamer Φ_1	rotamer Φ_2	multiplicity	partition fcn[a,b]	av energy,[a] kcal/mol	$\langle\Phi_1\rangle$	$\langle\Phi_2\rangle$
t^-	t^-	2	0.692	0.28	−38	−38
t^0	t^-	4	0.834	0.14	0	−38
t^+	t^-	2	0.704	0.27	38	−38
t^0	t^0	1	1.	0.	0	0
t^-	g^+	4	0.543	0.94	−38	89
t^0	g^+	4	0.630	0.83	0	89
t^+	g^+	4	0.519	0.97	38	89
g^+	g^+	2	0.393	1.65	89	89
g^+	g^-	2	0.339	1.54	84	−84

[a] Partition functions and energies are given relative to the t^0t^0-conformation. [b] Integral of $\exp(-E/kT)$ over the conformational domain of the rotamer.

Bonds 1, 2, ..., n are identical with skeletal bonds in polyethylene.[29]

An RIS model for ethylene–carbon monoxide copolymers was constructed following well-established methods.[30,31] For the CH_2–CH_2 bonds three approximately staggered conformations are appropriate. At first, rotation about the CO–CH_2 bond was subdivided into the same three isomeric states, but in the course of the calculations it became clear that the trans region could not be satisfactorily modeled by a single conformation. The region was consequently split into three equal domains, so that five rotational isomeric states resulted: "gauche minus" (g^-, −180° to −60°), "trans minus" (t^-, −60° to −20°), "trans" (t^0, −20° to 20°), "trans plus" (t^+, 20° to 60°), and "gauche plus" (g^+, 60° to 180°). Angles were then calculated for the three model compounds by integration over the resulting conformational domains at 400 K. Results are given in Tables V–VII. Subsequently, the partition functions from Tables V–VII were fitted into a set of statistical weight parameters, each of which stands for a certain type of interaction.[32] The following parameters were used,[33] subscripts denoting the type of bonds the statistical weight parameters refer to. The statistical weight matrices are shown in Table VIII.

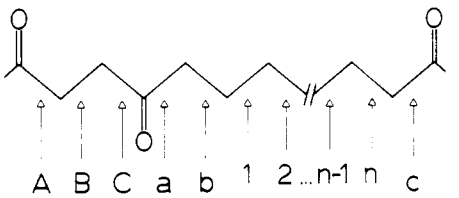

Figure 5. Designation of the bonds for the RIS scheme for ethylene–carbon monoxide copolymers.

Matrices a, b, and c (see Figure 5).

σ_a: First-order parameter describing the propensity for either of the two gauche states g^+ and g^- of the CO–CH_2 bond over the t^0-state.

λ: First-order parameter describing the likelihood of either a t^-- or a t^+-state of the CO–CH_2 bonds of over the t^0-state.

σ_b: First-order parameter describing the propensity for either of the two gauche states g^+ and g^- of the CH_2–CH_2 bond over the t-state.

ω_{ab}: Second-order parameter arising from the combination of gauche states of opposite signs of the CO–CH_2

Table VII
Integration Results for the 24 Distinguishable Rotamers of 2,5-Hexanedione

rotamer Φ_1	rotamer Φ_2	rotamer Φ_3	multiplicity	partition fcn[a,b]	av energy,[a] kcal/mol	dipole moment $\langle\mu^2\rangle_i^{0.5}$, D	$\langle\Phi_1\rangle$	$\langle\Phi_2\rangle$	$\langle\Phi_3\rangle$
t^-	t	t^-	2	0.1086	1.49	2.62	−34	1	−34
t^-	t	t^0	2	0.3417	0.73	1.59	−34	0	0
t^-	t	t^+	2	0.1269	1.42	0.98	−34	0	34
t^0	t	t^0	1	1.	0.	0.95	0	0	0
t^-	t	g^+	4	0.0265	3.13	2.19	−34	0	84
t^0	t	g^+	4	0.0671	2.49	3.13	0	−1	84
t^+	t	g^+	4	0.0210	3.29	3.91	34	−1	84
t^-	g^+	t^-	2	0.1146	1.37	2.31	−34	115	−34
t^-	g^+	t^0	4	0.2829	0.74	3.15	−35	113	−1
t^-	g^+	t^+	4	0.0687	1.71	4.01	−36	110	32
t^0	g^+	t^0	2	0.5137	0.32	3.64	−2	109	−2
t^0	g^+	t^+	4	0.0966	1.46	4.34	−3	105	32
t^+	g^+	t^+	2	0.0170	2.78	4.84	33	102	33
t^-	g^+	g^+	4	0.0091	3.93	4.97	−35	110	85
t^0	g^+	g^+	4	0.0168	3.63	5.24	−1	109	89
t^+	g^+	g^+	4	0.0058	4.50	5.24	35	113	93
t^-	g^+	g^-	4	0.0188	3.02	2.07	−33	114	−78
t^0	g^+	g^-	4	0.0595	2.24	3.08	0	114	−78
t^+	g^+	g^-	4	0.0185	3.05	3.85	33	112	−79
g^+	t	g^+	2	0.0044	5.08	4.46	85	−1	85
g^+	t	g^-	2	0.0062	4.77	1.34	85	0	−85
g^+	g^+	g^+	2	0.0024	5.60	4.73	89	115	89
g^+	g^+	g^-	4	0.0025	5.11	4.42	82	109	−80
g^+	g^-	g^+	2	0.0022	4.74	1.13	75	−112	75

[a] Partition functions and energies relative to the t^0tt^0-conformation. [b] Integral of $\exp(-E/kT)$ over the conformational domain of the rotamer.

Table VIII
Statistical Weight Matrices for the Conformational Analysis of Ethylene-Carbon Monoxide Copolymers[a]

bond type	$CO-C_2H_4-CO$	$CO-(C_2H_4)_{>1}-CO$
1, 2, ...		$\mathbf{U}_x = \begin{bmatrix} 1 & \sigma_{PE} & \sigma_{PE} \\ 1 & \sigma_{PE} & \sigma_{PE}\omega_{PE} \\ 1 & \sigma_{PE}\omega_{PE} & \sigma_{PE} \end{bmatrix}$
A, a	$\mathbf{U}_A = \begin{bmatrix} 1 & 1 & 1 & \sigma_A & \sigma_A \\ 1 & 1 & 1 & \sigma_A & \sigma_A \\ 1 & 1 & 1 & \sigma_A & \sigma_A \\ 1 & 1 & 1 & \sigma_A & \sigma_A \\ 1 & 1 & 1 & \sigma_A & \sigma_A \end{bmatrix}$	$\mathbf{U}_a = \begin{bmatrix} \lambda & 1 & \lambda & \sigma_a & \sigma_a \\ \lambda & 1 & \lambda & \sigma_a & \sigma_a \\ \lambda & 1 & \lambda & \sigma_a & \sigma_a \\ \lambda & 1 & \lambda & \sigma_a & \sigma_a \\ \lambda & 1 & \lambda & \sigma_a & \sigma_a \end{bmatrix}$
B, b	$\mathbf{U}_B = \begin{bmatrix} \kappa_{AB} & \sigma_B\kappa'_{AB} & \sigma_B\kappa''_{AB} \\ 1 & \sigma_B & \sigma_B \\ \kappa_{AB} & \sigma_B\kappa''_{AB} & \sigma_B\kappa'_{AB} \\ 1 & \sigma_B\psi & \sigma_B\omega_{AB} \\ 1 & \sigma_B\omega_{AB} & \sigma_B\psi \end{bmatrix}$	$\mathbf{U}_b = \begin{bmatrix} 1 & \sigma_b & \sigma_b \\ 1 & \sigma_b & \sigma_b \\ 1 & \sigma_b & \sigma_b \\ 1 & \sigma_b & \sigma_b\omega_{ab} \\ 1 & \sigma_b\omega_{ab} & \sigma_b \end{bmatrix}$
C, c	$\mathbf{U}_c = \begin{bmatrix} \kappa_{AB} & 1 & \kappa_{AB} & \sigma_A & \sigma_A \\ \kappa'_{AB} & 1 & \kappa''_{AB} & \sigma_A\psi & \sigma_A\omega_{AB} \\ \kappa''_{AB} & 1 & \kappa'_{AB} & \sigma_A\omega_{AB} & \sigma_A\psi \end{bmatrix}$	$\mathbf{U}_c = \begin{bmatrix} \kappa_{ab} & 1 & \kappa_{ab} & \sigma_a & \sigma_a \\ \kappa_{ab} & 1 & \kappa_{ab} & \sigma_a & \sigma_a\omega_{ab} \\ \kappa_{ab} & 1 & \kappa_{ab} & \sigma_a\omega_{ab} & \sigma_a \end{bmatrix}$

[a] Rows and columns are given in the order (t^-), t or t^0, (t^+), g^+, g^-.

and the CH_2–CH_2 bond ($g^{\pm}g^{\mp}$).

κ_{ab}: Second-order parameter arising from the combination of either a t^-- or a t^+-state of the CO–CH_2 bond with the CH_2–CH_2 bond in the trans conformation ($t^{\pm}t$ and $tt^{\pm}$).

κ'_{ab}: Second-order parameter that results from the combination of either a t^-- or a t^+-state of the CO–CH_2 bond with the CH_2–CH_2 bond in a gauche conformation of opposite sign ($t^{\pm}g^{\mp}$ and $g^{\pm}t^{\mp}$).

κ''_{ab}: Second-order parameter that is due to the combination of either a t^-- or a t^+-state of the CO–CH_2 bond with the CH_2–CH_2 bond in a gauche conformation of equal sign ($t^{\pm}g^{\pm}$ and $g^{\pm}t^{\pm}$).

Matrices A, B, and C (see Figure 5).

σ_A: First-order parameter describing the likelihood of either of the two gauche states g^+ and g^- of CO–CH_2 bonds over any of the trans states.

σ_B: First-order parameter describing the propensity for either of the two gauche states g^+ and g^- of the CH_2–CH_2 bond over the t-state.

ω_{AB}: Second-order parameter that results from the combination of gauche states of opposite signs of the CH_2–CH_2 and the CO–CH_2 bond ($g^{\pm}g^{\mp}$).

ψ: Second-order parameter arising from the combination of gauche states of equal signs of the CH_2–CH_2 and the CO–CH_2 bond ($g^{\pm}g^{\pm}$).

κ_{AB}: Second-order parameter arising from the combination of either a t^- or a t^+-state of the CO–CH_2 bond with the CH_2–CH_2 bond in trans conformation ($t^{\pm}t$ and $tt^{\pm}$).

κ'_{AB}: Second-order parameter that is due to the combination of either a t^-- or a t^+-state of the CO–CH_2 bond with the CH_2–CH_2 bond in a gauche conformation of opposite sign ($t^{\pm}g^{\mp}$ and $g^{\pm}t^{\mp}$).

κ''_{AB}: Second-order parameter that results from the combination of either a t^-- or a t^+-state of the CO–CH_2 bond with the CH_2–CH_2 bond in a gauche conformation of equal sign ($t^{\pm}g^{\pm}$ and $g^{\pm}t^{\pm}$).

In the above parameter set the letters σ and ω are employed analogously to common use in the literature.[30] The letter κ and λ have been chosen here to denote the interactions which were brought forth with the introduction of three different states in the range of the classical trans conformation and stand for the differences in energy of a t^-- or a t^+-state with respect to the t^0-state.

The third-order interaction of the two carbonyl groups in 2,5-hexanedione has been reduced to an effective second-order parameter, which was denoted ψ. If two neighboring bonds in 2,5-hexanedione both are in a gauche state of the same sign, a situation results, as can be seen from inspections of models, where the two carbonyl groups are always in more or less parallel position with respect to each other, regardless of the state of the third bond. Therefore, the resulting repulsive interaction can be described approximately with a second-order parameter, the values of all other parameters being slightly adjusted. Thus, the parameters used with isolated ethylene units bear some of the effect of carbonyl–carbonyl interaction.

Table IX
Numerical Values of Statistical Weight Parameters

$\xi = \xi_0 \exp(-E_\xi/RT)$	ξ_0	E_ξ, kcal/mol
σ_b	0.7	0.7
σ_a	1.7	0.9
ω_{ab}	0.9	0.0
κ_{ab}	0.8	0.2
κ'_{ab}	1.5	0.0
κ''_{ab}	1.1	0.5
λ	1.0	0.1
σ_B	0.8	0.3
σ_A	1.6	2.5
ω_{AB}	0.8	-0.6
ψ	1.3	0.8
κ_{AB}	0.8	0.7
κ'_{AB}	0.9	0.4
κ''_{AB}	0.8	1.1
σ_{PE}	1.0	0.5[a]
ω_{PE}	1.0	2.0[a]

[a] Reference 29.

Table X
Comparison of the Rotamer Population of 2-Pentanone at 400 K; Direct Integration and RIS Values

rotamers				statistical wt params	rotamer population	
Φ_1	Φ_2	Φ_1	Φ_2		direct integratn	RIS model
t^-	t	t^+	t	κ_{ab}	13.2%	10.6%
t^0	t				17.5%	18.2%
t^-	g^+	t^+	g^-	σ_b, κ'_{ab}	5.7%	7.7%
t^0	g^+	t^0	g^-	σ_b	5.0%	5.3%
t^+	g^+	t^-	g^-	σ_b, κ''_{ab}	3.0%	3.1%
g^+	t	g^-	t	σ_a	8.5%	9.1%
g^+	g^+	g^-	g^-	σ_a, σ_b	3.4%	2.6%
g^+	g^-	g^-	g^+	σ_a, σ_b, ω_{ab}	2.5%	2.5%

Table XI
Comparison of the Rotamer Population of 3-Pentanone at 400 K; Direct Integration and RIS Values

rotamers								statistical wt params	rotamer population: direct integratn	rotamer population: RIS model
Φ_1	Φ_2	Φ_1	Φ_2	Φ_1	Φ_2	Φ_1	Φ_2			
t^-	t^-	t^+	t^+					λ, λ	4.5%	4.6%
t^-	t^0	t^0	t^-	t^0	t^+	t^+	t^0	λ	5.4%	5.5%
t^-	t^+	t^+	t^-					λ, λ	4.6%	4.6%
t^0	t^0								6.5%	6.5%
t^-	g^+	t^+	g^-	g^+	t^-	g^-	t^+	σ_a, λ	3.5%	3.4%
t^0	g^+	t^0	g^-	g^+	t^-	g^-	t^+	σ_a	4.1%	4.1%
t^-	g^-	t^+	g^+	g^+	t^+	g^-	t^-	σ_a, λ	3.4%	3.4%
g^+	g^+	g^-	g^-					σ_a, σ_a	2.6%	2.6%
g^+	g^-	g^-	g^+					σ_a, σ_a	2.2%	2.2%

Table XII
Comparison of the Rotamer Population of 2,5-Hexanedione at 400 K; Direct Integration and RIS Values

rotamer			multiplicity	statistical wt params	rotamer population: direct integratn	rotamer population: RIS model
Φ_1	Φ_2	Φ_3				
t^-	t	t^-	2	κ_{AB}, κ_{AB}	1.73%	1.83%
t^-	t	t^0	2	κ_{AB}	5.45%	5.38%
t^-	t	t^+	2	κ_{AB}, κ_{AB}	2.03%	1.83%
t^0	t	t^0	1		16.0%	15.8%
t^-	t	g^+	4	σ_A, κ_{AB}	0.42%	0.36%
t^0	t	g^+	4	σ_A	1.07%	1.06%
t^+	t	g^+	4	σ_A, κ_{AB}	0.34%	0.36%
t^-	g^+	t^-	2	σ_B, κ'_{AB}, κ'_{AB}	1.83%	2.57%
t^-	g^+	t^0	4	σ_B, κ'_{AB}	4.61%	4.58%
t^-	g^+	t^+	4	σ_B, κ'_{AB}, κ''_{AB}	1.10%	0.86%
t^0	g^+	t^0	2	σ_B	8.20%	8.14%
t^0	g^+	t^+	4	σ_B, κ''_{AB}	1.54%	1.53%
t^+	g^+	t^+	2	σ_B, κ''_{AB}, κ''_{AB}	0.27%	0.29%
t^-	g^+	g^+	4	σ_B, σ_A, ψ, κ'_{AB}	0.15%	0.15%
t^0	g^+	g^+	4	σ_B, σ_A, ψ	0.27%	0.27%
t^+	g^+	g^+	4	σ_B, σ_A, ψ, κ''_{AB}	0.093%	0.050%
t^-	g^+	g^-	4	σ_B, σ_A, ω_{AB}, κ'_{AB}	0.30%	0.53%
t^0	g^+	g^-	4	σ_B, σ_A, ω_{AB}	0.95%	0.94%
t^+	g^+	g^-	4	σ_B, σ_A, ω_{AB}, κ''_{AB}	0.29%	0.18%
g^+	t	g^+	2	σ_A, σ_A	0.070%	0.071%
g^+	t	g^-	2	σ_A, σ_A	0.099%	0.071%
g^+	g^+	g^+	2	σ_B, σ_A, σ_A, ψ, ψ	0.038%	0.009%
g^+	g^+	g^-	4	σ_B, σ_A, σ_A, ω_{AB}, ψ	0.040%	0.031%
g^+	g^-	g^+	2	σ_B, σ_A, σ_A, ω_{AB}, ω_{AB}	0.035%	0.109%

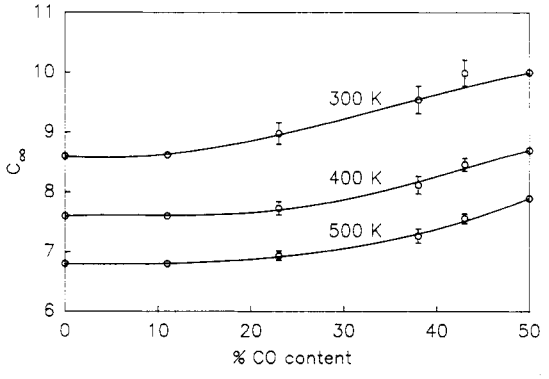

Figure 6. Calculated characteristic ratios of the mean-square end-to-end distance of semialternating ethylene–carbon monoxide copolymers as a function of carbon monoxide content and temperature. Error bars indicate 95% confidence levels.

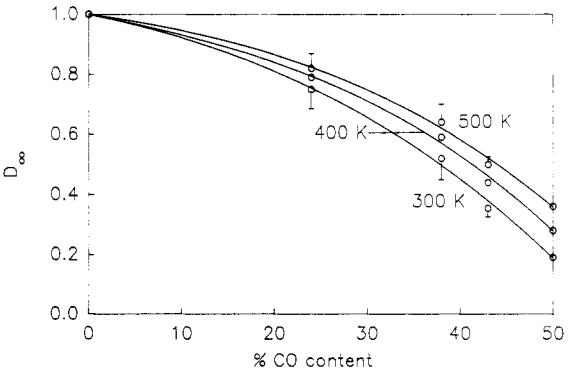

Figure 7. Calculated mean-square dipole moment ratios of semialternating ethylene–carbon monoxide copolymers as a function of carbon monoxide content and temperature. Error bars indicate 95% confidence levels.

In Table IX the estimated values for the different parameters are given and in Tables X–XII the statistical weights for individual conformers obtained with the parameterized model are compared to those obtained by direct integration. Torsion angles assigned to the different rotational isomeric states were, t^0, 0°; $t^{\pm}$, ±35°; $g^{\pm}$, ±90° (bonds A, a, C, and c); ±110° (bonds B and b); and ±120° (bonds 1, 2, ..., n).

Figure 6 gives the characteristic ratio of the mean-square end-to-end distance of infinitely long chains for copolymers of different carbonyl content computed following ref 31. The values were obtained by averaging over Monte Carlo ensembles of 100 different structures. The sequences of these chains were generated by using statistics developed above ("first-order Markov" statistics were assumed, obtained by setting $q_{Et} = q'_{Et}$ in eq 2). The temperature coefficient $d(\ln C_\infty)/dT$ for the range 300–500 K is –0.0013 K^{-1}, independent of the carbonyl content. The rough experimental estimate mentioned above (8.5 ∓ 1.5 at 25 °C) is consistent with these values.

Figure 7 shows the results for the characteristic ratio of the mean-square dipole moment.[31] Its temperature coef-

Table XIII
Comparison of Computed Dipole Moment of 2,5-Hexanedione, $\langle\mu^2\rangle^{0.5}$, with Experiment

	300 K	400 K	500 K
calcd			
direct integratn	2.7 D	2.9 D	3.0 D
RIS model	2.8 D	2.9 D	3.0 D
exptl	3.05 D (333 K, dioxane)		

ficients $d(\ln D_\infty)/dT$ for the range 300–500 K are 0.000 45, 0.0010, 0.0018, and 0.0032 K^{-1}, respectively, for carbonyl contents of 24, 38, 43, and 50%, respectively. The values of D_∞ being less than unity reflects the tendency of the carbonyl groups to be in antiparallel position. Perfect antiparallel alignment would yield a value of zero and occurs in chains or sequences where all the bonds are in the trans conformation. The calculation above showed that this is the most stable conformation of the chain. The positive temperature coefficient is therefore due to the loss of antiparallel correlation mainly because of increased population of gauche states with higher temperature. Increase of the average length of the ethylene sections separating carbonyl groups also decreases this correlation and D_∞ reaches the limiting value of unity (completely uncorrelated) for polyethylene.

Comparison between Calculations and Experiment. Usually, the chain conformation of lowest energy is also the one found in the crystalline state. The calculations reported above show that this is the zigzag planar conformation with all torsion angles in the t- or t^0-state in accordance with X-ray diffraction results.[11]

For qualitative comparison the dipole moment of 2,5-hexanedione was calculated first. Because there are only three degrees of freedom (Φ_1, Φ_2, Φ_3) in this case, the same quantity has also been calculated by integration over conformation space. The comparison of this result with experiment tests the quality of the applied force field; a comparison with the RIS model tests the choice of rotational isomeric states. The values given in Table XIII indicate excellent agreement between the RIS model and direct integration and substantial agreement with experiment.

Furthermore, the ratio of the mean-square dipole moment was calculated for chains having the same composition and average molecular weights as those that were used for the dipole moment measurements. The structure of these chains was chosen to match the actual structure as determined by ^{1}H NMR spectra, using the "second-order Markov" statistics given in Table II. The results for the dipole moment ratio calculations are given in Table XIV.

In Table XIV the calculated and experimentally determined values of the mean-square dipole moment ratios of the two semialternating copolymer samples are listed. The calculated values depend somewhat on the assumed molecular weight distribution of the sample, which is not known for the experiment. In spite of this uncertainty, one has to judge the agreement between experiment and calculations for the dipole moment ratios as good. As mentioned before, some experimental evidence exists that the characteristic ratio of the unperturbed mean-square end-to-end distance of the alternating ethylene–carbon monoxide copolymer lies in the range 8.5 ∓ 1.5 at 25 °C. This is consistent with the value of about 10 calculated for a completely alternating copolymer.

Conclusions

At first glance, the RIS model presented here seems to be rather complicated with regard to the number of rotational isomeric states per bond and the number of different parameters used. However, calculations of mean-square end-to-end distances using a model with just three different rotational isomeric states for each bond yielded values which were considerably higher than those obtained with the model presented here and clearly in disagreement with the (admittedly incomplete) experimental value. It was realized that the width of the potential energy well around the $CO–CH_2$ bonds make three states at 0°, ∓120° inadequate (the introduction of more than three states around the $CH_2–CH_2$ bonds has only negligible effect on the values of the calculated quantities).

The introduction of the pseudo-second-order parameter ψ, which accounts for the main part of the carbonyl–carbonyl interaction in a $CO–C_2H_4–CO$ sequence (which is of third order), and the adjustments that follow in the rest of the parameters had as a consequence that one has to use different parameters for interactions of seemingly identical type in these and in $CO–(C_2H_4)_{>1}–CO$ sequences. Thus the number of necessary parameters is doubled. Another possibility would have been to use third-order parameters for the carbonyl–carbonyl interaction. This would have substantially increased the complexity of calculations by increasing the dimension of the statistical weight matrices. The model presented here uses a small number of rotational isomeric states and a manageable number of parameters and yields satisfactory results; comparison of calculations with experimental data shows very good agreement. It must be noted that in all computations presented here no "adjustable parameter" has been used to fit calculations to experiment.

Although there are not enough experimental results available to date to rigorously test the validity of this RIS scheme, one can draw some preliminary conclusions on the conformation of ethylene–carbon monoxide copolymers. Figure 6 shows that the introduction of isolated carbonyl groups into a polyethylene chain has virtually no effect on the chain dimensions. The unperturbed dimensions of an alternating ethylene–carbon monoxide copolymer chain are

Table XIV
Comparison of the Calculated Dipole Moment Ratios for the Two Ethylene–Carbon Monoxide Copolymer Samples with Experimental Results

					rel ^{1}H NMR signal int						
	% CO	M_n	M_w	M_w/M_n	A	B	C	D	E	F	$\langle\mu^2\rangle/n_k\langle\mu^2\rangle_{CO}$
					Acetone Sol Fract (p_{Et}^t, 0.061; q_{Et}, 0.21; q'_{Tt}, 0.54)[a]						
calcd	40.3	870	1440	1.7	1.0	0.58	0.49	0.14	0.13	0.06	0.51 ∓ 0.02
	40.3	890	1760	2.0	1.0	0.57	0.49	0.14	0.13	0.06	0.55 ∓ 0.02
exptl	40.3	880			1.0	0.58	0.49	0.13	0.15	0.04	0.43 ∓ 0.03
					Dipropyl Ket Sol Fract (p_{Et}^t, 0.0365; q_{Et}, 0.17; q'_{Et}, 0.37)[a]						
calcd	42.6	1730	2370	1.4	1.0	0.40	0.36	0.07	0.06	0.02	0.41 ∓ 0.01
	42.6	1720	3240	1.9	1.0	0.40	0.36	0.08	0.06	0.02	0.45 ∓ 0.01
exptl	42.6	1730			1.0	0.41	0.36	0.07	0.06	0.02	0.42 ∓ 0.03

[a] p_{Et}^t, q_{Et}, q'_{Et}: probabilities for the Markov generation of the monomer sequence in the model chains (see Table II).

of about the same order of magnitude as those of a polyethylene chain. The insolubility of the alternating ethylene–carbon monoxide copolymer therefore seems to be due mainly to a high packing energy in the crystal, which arises from the regular repetition of keto groups along the hydrocarbon chain. The increase in packing energy is reflected by the melting point difference of roughly 100 deg between polyethylene (≈138 °C) and the alternating ethylene–carbon monoxide copolymer (≈254 °C). The same effect can be observed by comparison of the melting points of low molecular model compounds such as propane (–190 °C) and acetone (–95 °C) or hexane (–95 °C) and 2,5-hexanedione (–8 °C). The interdependence of solubility and melting point is further demonstrated by the copolymer samples used for dipole moment measurements. They were soluble in dioxane at 60 °C and accordingly showed melting points of only 101 and 141 °C, respectively.

Acknowledgment. We thank Dr. Keizo Matsuo for invaluable assistance and advice with the dielectric constant measurements.

Registry No. (CO)(Et) (alternating copolymer), 111190-67-1; 3-pentanone, 96-22-0; 2-pentanone, 107-87-9; 2,5-hexanedione, 110-13-4.

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