Macromolecules 1981, *14*, 523–528

conventional PGC and PHGC with catalytic hydrogenation.

The fact that there exists fairly good agreement between the relative yields before and after hydrogenation supports the validity of the presumption for the assignment of some peaks on the pyrogram in Figure 1A. Thus, the identified peaks in the monomer and the trimer regions on the pyrograms in Figures 1A and 1B mostly reflect the H–H and/or the T–T structures. Although the monomer is still most abundant among the products on the pyrogram, its yield only amounts to 20.4%. On the other hand, the formation of a comparable size for the multiplets of the monomer, dimer, and trimer regions suggests that random scission type thermal degradation might be predominant for H–H PS.

As was reported in the PMS work on H–H PS by Lüderwald,[6] we can also find on the pyrogram in Figure 1B a very minor $PhCH_2Ph$ peak (peak 10) and a fairly strong $PhCH(CH_3)Ph$ peak (peak 35). This suggests either that these structures were incorporated through minor byproducts at the stage of the monomer preparation or that thermal rearrangements took place during the pyrolysis. Furthermore, it is very interesting to note that, even though very minor, $PhCH_2CH_2Ph$ and $PhCH_2CHPhCH_3$ peaks can be observed on the pyrogram of H–T PS (Figure 1C). This fact, which was also pointed out by Alajbeg et al.,[13] could be indicative of the existence of H–H linkages even in H–T PS.

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Epimerization of Vinyl Polymers to Stereochemical Equilibrium.

1. Theory[1]

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ABSTRACT: Flory's theory of stereochemical equilibrium in vinyl polymers is generalized. Equilibrium frequencies for stereochemical sequences of any length (m-ads) in chains of any length x can be obtained with the new formulation; the calculated frequency is averaged over the entire length of the chains. Some numerical results for sequences up to $m = 5$ (pentads) are presented, and it is demonstrated that the dyad distribution in vinyl chains at equilibrium does not follow any type of unidirectional statistics, e.g., any order Markoff.

Introduction

Vinyl polymers exist in a potentially extraordinarily large number of diastereomers. We will consider chains of the general formula

$$CH_3\text{–}(CHRCH_2)_x\text{–}H \qquad (1)$$

Under conditions where the diastereomers are epimerized to stereochemical equilibrium, the different diastereomers occur in fractions that are proportional to their partition functions. Although the large number of diastereomers quickly precludes resolution of diastereomers as x exceeds all but the smallest values, the frequency of occurrence of diastereomeric substructures comprising m monomeric units, m-ads, can often still be analytically determined. These frequencies are proportional to the sum over all the appropriate partition functions of the chains that contain the specified substructure, taken as many times as the substructure occurs in the chain. When the basic assumptions of rotational isomeric state models are accepted, it can be shown that the only relevant terms in the partition functions are the ones pertaining to conformation.

In 1967 Flory[2] formulated the concept of the method and presented a formulation that yields the frequency of occurrence of dyads and triads in chains of any length at stereochemical equilibrium, averaged along the chains (and over all chains), the only parameters required being the statistical weight parameters that govern the conformational equilibria. His comparison with some of the data from the first experiments of this kind carried out by Clark[3] with derivatives of 2,4-dicarboxypentane and 2,4,6-tricarboxyheptane (as model compounds for the corresponding polyacrylates) gave satisfactory agreement. Since then, the method has been applied to equilibria in low molecular weight model compounds of vinyl polymers ($x = 2$ and 3, except for the polypropylene models, where $x = 4$ and 5) in a number of cases,[4-12] mostly in order to obtain information on conformational statistical weight parameters.

Polymers have resisted epimerization without side reactions until recently. Suter[13] and others[14] succeeded in transforming isotactic polypropylene to ether-soluble "atactic" products as early as 1970, but stereochemical equilibrium was not reached. The first apparently successful equilibrium epimerization was published in 1979 by Shepherd, Chen, and Harwood;[15,16] these authors reported on the epimerization of isotactic polystyrene to a product with the same ^1H NMR spectrum as atactic polystyrene (the triad frequencies were estimated, using their data, to be $f_{mm} \approx 0.2$, $f_{mr} \approx 0.5$, and $f_{rr} \approx 0.3$; $f_m \approx 0.45$).

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Table I
Reported Stereochemical Equilibria in Compounds of the Type CH_3-$(CHRCH_2)_x$-H

R	T, °C	solvent	catalyst	x	f_m	f_{mm}	f_{mr}	f_{rr}	ref
CN	25	MeOH	NaOH	2	0.40				3
COOMe	25	MeOH	MeONa	2	0.455				3
				3	0.453	0.198	0.509	0.293	3
COOEt	25	EtOH	EtONa	3	0.431	0.178	0.506	0.314	3
COO-*i*-Pr	25	*i*-PrOH	*i*-PrONa	3	0.360	0.117	0.485	0.398	3
COOH	180	H_2O	HCl	3	0.483	0.242	0.482	0.274	3
$COONH_4$	180	H_2O	NH_4OH	3	0.487	0.244	0.486	0.271	3
COONa	180	H_2O	NaOH	3	0.449	0.197	0.504	0.299	3
Ph	25	Me_2SO	*t*-BuOK	2	0.486				4
	70	Me_2SO	*t*-BuOK	3	0.467	0.217	0.499	0.284	5
	100	HMPA	*t*-BuOK	∞	~0.45	~0.20	~0.50	~0.30	15
2-pyridyl		Me_2SO	*t*-BuOK	2	~0.5				10
	25	Me_2SO	*t*-BuOK	3	~0.5	~0.25	~0.5	~0.25	11
Cl	25	CS_2	$AlCl_3$	2	0.29				7
	70	Me_2SO	LiCl	2	0.364				6
	70	Me_2SO	LiCl	3	0.342	0.111	0.462	0.427	8
$COC(CH_3)_3$	100	*o*-DCB	*t*-BuOK/18-crown-6	2	0.600				12
	150	*o*-DCB	*t*-BuOK/18-crown-6	2	0.578				12
	150	*o*-DCB	*t*-BuOK/18-crown-6	3	0.585	0.349	0.472	0.179	12
CH_3	−75	pentane	$ClSO_3H$	4	0.459				9
	270	octane	Pd/C	4	0.485				9
	270	octane	Pd/C	5	0.487	0.237	0.500	0.263	9

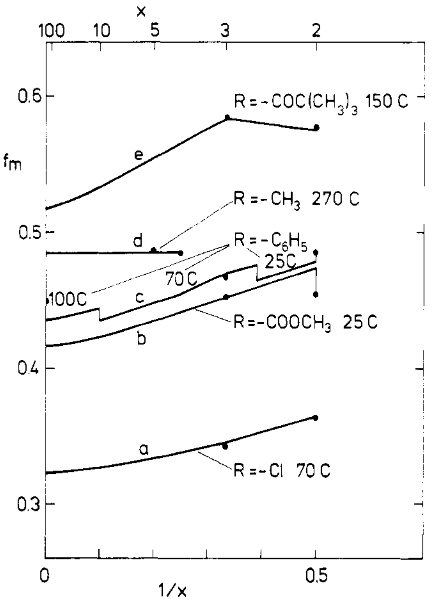

Figure 1. Reported dyad frequencies f_m for chains for which also rotational isomeric state models are known. (●) Experimental data from Table I. Statistical weight parameters from: (a) ref 8; (b) Yoon, D. Y.; Suter, U. W.; Sundararajan, P. R.; Flory, P. J. *Macromolecules* **1975**, *8*, 784–9; (c) Yoon, D. Y.; Sundararajan, P. R.; Flory, P. J. *Ibid.* **1975**, *8*, 776–83; (d) Suter, U. W.; Flory, P. J. *Ibid.* **1975**, *8*, 765–76; (e) ref 12.

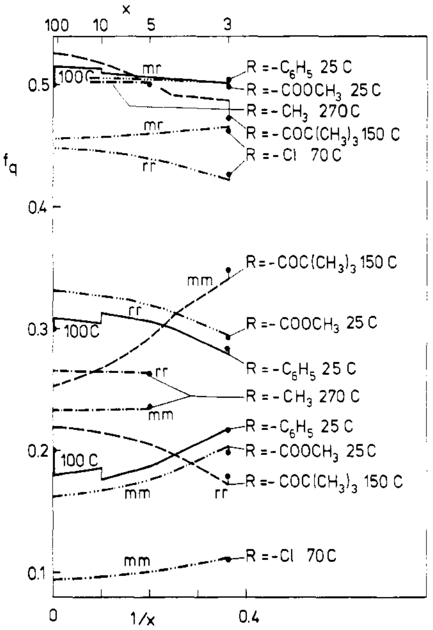

Figure 2. Reported triad frequencies f_{mm}, f_{mr}, and f_{rr} for chains for which also rotational isomeric state models are known. (●) Experimental data from Table I. Sources of statistical weight parameters are the same as for Figure 1.

All data known to the author to date are collected in Table I and in Figures 1 and 2. The lines plotted in these figures are calculated with Flory's theory,[2] using the parameters given in the literature indicated. Note that convergence of the equilibrium fractions to the values for $x \to \infty$ is quite fast.

Today the improvement of analytical methods, especially of NMR spectroscopy, allows experimental determination of longer sequences. Pentads and longer sequences have been resolved in several cases and even complete assignment of pentads has been accomplished. Hence, Flory's theory should be generalized. In one instance, with polypropylene, we have succeeded in achieving stereochemical equilibrium with the polymer, and the equilibrium frequencies of the pentads have been determined as will be described in the following paper.[17] In this paper we present the general theory for *m*-ads of any length in chains of any length.

A Priori Probabilities of Diastereomeric Sequences

Vinyl polymer chains consist of constitutionally identical segments comprising one backbone bond each that differ only in their orientation along the chain. Interactions beyond second order in the main chain may usually be ignored and the conformational characteristics of the polymer backbone are fully defined by the statistical weight matrices **U**′ and **U**″,[18,19] one for each of the two types of chain segments that differ in orientation along the chain. If three rotational states may be assumed, **U**′ may often be written as[19]

$$\mathbf{U}' = \begin{bmatrix} 1 & 1 & 1 \\ 1 & 0 & 1 \\ 1 & 1 & 0 \end{bmatrix} \qquad (2)$$

Table II
Matrices W'_q for Sequence Lengths $m = 3$, 4, and 5[a]

$m = 3$

$$W'_{\mathrm{mm}} = \begin{bmatrix} \mathbf{U}_\mathrm{m}^{(2)} & \cdot \\ \cdot & \end{bmatrix} \qquad W'_{\mathrm{mr}} = \begin{bmatrix} \cdot & \mathbf{U}_\mathrm{r}^{(2)} \\ \mathbf{U}_\mathrm{m}^{(2)} & \cdot \end{bmatrix} \qquad W'_{\mathrm{rr}} = \begin{bmatrix} & \cdot \\ \cdot & \mathbf{U}_\mathrm{r}^{(2)} \end{bmatrix}$$

$m = 4$

$$W'_{\mathrm{mmm}} = \begin{bmatrix} \mathbf{U}_\mathrm{m}^{(2)} & \cdot & \cdot & \cdot \\ \cdot & & & \\ \cdot & & & \\ \cdot & & & \end{bmatrix} \qquad W'_{\mathrm{mmr}} = \begin{bmatrix} \cdot & \mathbf{U}_\mathrm{r}^{(2)} & \cdot & \cdot \\ \cdot & \cdot & & \\ \mathbf{U}_\mathrm{m}^{(2)} & \cdot & \cdot & \cdot \\ \cdot & \cdot & & \end{bmatrix}$$

$$W'_{\mathrm{mrm}} = \begin{bmatrix} & & \cdot & \\ \cdot & \cdot & \mathbf{U}_\mathrm{m}^{(2)} & \cdot \\ & & \cdot & \\ & & \cdot & \end{bmatrix} \qquad W'_{\mathrm{mrr}} = \begin{bmatrix} & & \cdot & \cdot \\ \cdot & \cdot & \cdot & \mathbf{U}_\mathrm{r}^{(2)} \\ & & \cdot & \cdot \\ \cdot & \cdot & \mathbf{U}_\mathrm{m}^{(2)} & \cdot \end{bmatrix}$$

$$W'_{\mathrm{rmr}} = \begin{bmatrix} & \cdot & & \\ & \cdot & & \\ \cdot & \mathbf{U}_\mathrm{r}^{(2)} & \cdot & \cdot \\ & \cdot & & \end{bmatrix} \qquad W'_{\mathrm{rrr}} = \begin{bmatrix} & & & \cdot \\ & & & \cdot \\ & & & \cdot \\ \cdot & \cdot & \cdot & \mathbf{U}_\mathrm{r}^{(2)} \end{bmatrix}$$

$m = 5$

$$W'_{\mathrm{mmmm}} = \begin{bmatrix} \mathbf{U}_\mathrm{m}^{(2)} & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & & & & & & & \\ \cdot & & & & & & & \\ \cdot & & & & & & & \\ \cdot & & & & & & & \\ \cdot & & & & & & & \\ \cdot & & & & & & & \\ \cdot & & & & & & & \end{bmatrix} \qquad W'_{\mathrm{mmmr}} = \begin{bmatrix} \cdot & \mathbf{U}_\mathrm{r}^{(2)} & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & & & & & & \\ \cdot & \cdot & & & & & & \\ \cdot & \cdot & & & & & & \\ \mathbf{U}_\mathrm{m}^{(2)} & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & & & & & & \\ \cdot & \cdot & & & & & & \\ \cdot & \cdot & & & & & & \end{bmatrix}$$

$$W'_{\mathrm{mmrm}} = \begin{bmatrix} & & \cdot & & \cdot & & & \\ \cdot & \cdot & \mathbf{U}_\mathrm{m}^{(2)} & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \mathbf{U}_\mathrm{m}^{(2)} & \cdot & \cdot & \cdot \\ & & \cdot & & \cdot & & & \\ & & \cdot & & \cdot & & & \\ & & \cdot & & \cdot & & & \\ & & \cdot & & \cdot & & & \\ & & \cdot & & \cdot & & & \end{bmatrix} \qquad W'_{\mathrm{mmrr}} = \begin{bmatrix} & & & \cdot & \cdot & & & \\ \cdot & \cdot & \cdot & \mathbf{U}_\mathrm{r}^{(2)} & \cdot & \cdot & \cdot & \cdot \\ & & & \cdot & \cdot & & & \\ & & & \cdot & \cdot & & & \\ & & & \cdot & \cdot & & & \\ & & & \cdot & \cdot & & & \\ \cdot & \cdot & \cdot & \cdot & \mathbf{U}_\mathrm{m}^{(2)} & \cdot & \cdot & \cdot \\ & & & \cdot & \cdot & & & \end{bmatrix}$$

$$W'_{\mathrm{mrmr}} = \begin{bmatrix} & & \cdot & & & \cdot & & \\ & & \cdot & & & \cdot & & \\ \cdot & \cdot & \cdot & \cdot & \cdot & \mathbf{U}_\mathrm{r}^{(2)} & \cdot & \cdot \\ & & \cdot & & & \cdot & & \\ & & \cdot & & & \cdot & & \\ \cdot & \cdot & \mathbf{U}_\mathrm{m}^{(2)} & \cdot & \cdot & \cdot & \cdot & \cdot \\ & & \cdot & & & \cdot & & \\ & & \cdot & & & \cdot & & \end{bmatrix} \qquad W'_{\mathrm{rmmr}} = \begin{bmatrix} & \cdot & & & & & & \\ & \cdot & & & & & & \\ & \cdot & & & & & & \\ & \cdot & & & & & & \\ \cdot & \mathbf{U}_\mathrm{r}^{(2)} & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ & \cdot & & & & & & \\ & \cdot & & & & & & \\ & \cdot & & & & & & \end{bmatrix}$$

$$W'_{\mathrm{mrrm}} = \begin{bmatrix} & & & & & & \cdot & \\ & & & & & & \cdot & \\ & & & & & & \cdot & \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \mathbf{U}_\mathrm{m}^{(2)} & \cdot \\ & & & & & & \cdot & \\ & & & & & & \cdot & \\ & & & & & & \cdot & \\ & & & & & & \cdot & \end{bmatrix} \qquad W'_{\mathrm{mrrr}} = \begin{bmatrix} & & & & & & \cdot & \cdot \\ & & & & & & \cdot & \cdot \\ & & & & & & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \mathbf{U}_\mathrm{r}^{(2)} \\ & & & & & & \cdot & \cdot \\ & & & & & & \cdot & \cdot \\ & & & & & & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \mathbf{U}_\mathrm{m}^{(2)} & \cdot \end{bmatrix}$$

$$W'_{\mathrm{rmrr}} = \begin{bmatrix} & & & \cdot & & \cdot & & \\ & & & \cdot & & \cdot & & \\ & & & \cdot & & \cdot & & \\ & & & \cdot & & \cdot & & \\ & & & \cdot & & \cdot & & \\ \cdot & \cdot & \cdot & \mathbf{U}_\mathrm{r}^{(2)} & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \mathbf{U}_\mathrm{r}^{(2)} & \cdot & \cdot \\ & & & \cdot & & \cdot & & \end{bmatrix} \qquad W'_{\mathrm{rrrr}} = \begin{bmatrix} & & & & & & & \cdot \\ & & & & & & & \cdot \\ & & & & & & & \cdot \\ & & & & & & & \cdot \\ & & & & & & & \cdot \\ & & & & & & & \cdot \\ & & & & & & & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \mathbf{U}_\mathrm{r}^{(2)} \end{bmatrix}$$

[a] Only nonzero elements are given, their positions being indicated by dots.

and $\mathbf{U}''$, depending upon the stereochemical character of the dyad (i.e., racemic or meso), as[19]

$$\mathbf{U}''_\mathrm{m} = \begin{bmatrix} \eta^2\omega'' & \eta & \eta\tau\omega' \\ \eta & \omega & \tau\omega' \\ \eta\tau\omega' & \tau\omega' & \tau^2\omega\omega'' \end{bmatrix} \tag{3}$$

or

$$\mathbf{U}''_\mathrm{r} = \begin{bmatrix} \eta^2 & \eta\omega' & \eta\tau\omega'' \\ \eta\omega' & 1 & \tau\omega \\ \eta\tau\omega'' & \tau\omega & \tau^2\omega'^2 \end{bmatrix} \tag{4}$$

These matrices can be formulated for any number ν of rotational isomeric states, however.

Dyad matrices may be defined for convenience for the two types of dyads

$$\mathbf{U}_\mathrm{m}^{(2)} = \mathbf{U}'\mathbf{U}''_\mathrm{m} \qquad \mathbf{U}_\mathrm{r}^{(2)} = \mathbf{U}'\mathbf{U}''_\mathrm{r} \tag{5}$$

The conformational partition function is[18]

$$Z = \mathbf{U}_0 \left[\prod_{1}^{x-1} \mathbf{U}_k^{(2)} \right] \mathbf{U}_x \tag{6}$$

Table III
Stereochemical Equilibrium for Three Sets of Statistical Weight Parameters ($\omega = 0$ for All)

	x				
	2	3	4	5	∞
		$\eta = 1, \tau^* = 1$			
f_{m}	$^{1}/_{2} = 0.500$	0.500	0.481	0.472	0.444
f_{mm}		$^{1}/_{4} = 0.250$	0.222	0.210	0.185
f_{mr}		$^{1}/_{2} = 0.500$	0.500	0.506	0.519
f_{rr}		$^{1}/_{4} = 0.250$	0.278	0.284	0.296
f_{mmm}			$^{1}/_{9} = 0.111$	0.093	0.074
f_{mmr}			$^{2}/_{9} = 0.222$	0.222	0.222
f_{mrm}			$^{5}/_{36} = 0.139$	0.130	0.123
f_{mrr}			$^{5}/_{18} = 0.278$	0.278	0.272
f_{rmr}			$^{1}/_{9} = 0.111$	0.130	0.148
f_{rrr}			$^{5}/_{36} = 0.139$	0.148	0.160
f_{mmmm}				$^{5}/_{108} = 0.046$	0.029
f_{mmmr}				$^{5}/_{54} = 0.093$	0.090
f_{mmrm}				$^{7}/_{54} = 0.130$	0.107
f_{mmrr}				$^{7}/_{54} = 0.130$	0.115
f_{mrmr}				$^{7}/_{54} = 0.130$	0.140
f_{rmmr}				$^{5}/_{108} = 0.046$	0.066
f_{mrrm}				$^{2}/_{27} = 0.074$	0.062
f_{mrrr}				$^{4}/_{27} = 0.148$	0.148
f_{rmrr}				$^{7}/_{54} = 0.130$	0.156
f_{rrrr}				$^{2}/_{27} = 0.074$	0.086
$4f_{\mathrm{mm}}f_{\mathrm{rr}}/f_{\mathrm{mr}}^{2}$		1	0.988	0.930	0.816
$\rho = 2f_{\mathrm{m}}f_{\mathrm{r}}/f_{\mathrm{mr}}$		1	0.999	0.985	0.952
$\Omega = f_{\mathrm{r}}f_{\mathrm{rrr}}/f_{\mathrm{rr}}^{2}$			0.867	0.868	0.812
$f_{\mathrm{mm}}f_{\mathrm{mmmm}}/f_{\mathrm{mmm}}^{2}$				1.134	0.972
		$\eta = 2, \tau^* = 1$			
f_{m}	$^{4}/_{9} = 0.444$	0.417	0.403	0.396	0.375
f_{mm}		$^{1}/_{6} = 0.167$	0.146	0.139	0.125
f_{mr}		$^{1}/_{2} = 0.500$	0.500	0.500	0.500
f_{rr}		$^{1}/_{3} = 0.333$	0.354	0.361	0.375
f_{mmm}			$^{1}/_{18} = 0.056$	0.049	0.039
f_{mmr}			$^{13}/_{72} = 0.181$	0.177	0.172
f_{mrm}			$^{17}/_{144} = 0.118$	0.109	0.102
f_{mrr}			$^{11}/_{36} = 0.306$	0.302	0.297
f_{rmr}			$^{5}/_{36} = 0.139$	0.151	0.164
f_{rrr}			$^{29}/_{144} = 0.201$	0.214	0.226
f_{mmmm}				$^{5}/_{288} = 0.017$	0.012
f_{mmmr}				$^{17}/_{288} = 0.059$	0.055
f_{mmrm}				$^{25}/_{288} = 0.087$	0.070
f_{mmrr}				$^{1}/_{9} = 0.111$	0.102
f_{mrmr}				$^{19}/_{144} = 0.132$	0.133
f_{rmmr}				$^{7}/_{144} = 0.049$	0.059
f_{mrrm}				$^{5}/_{72} = 0.069$	0.059
f_{mrrr}				$^{53}/_{288} = 0.184$	0.180
f_{rmrr}				$^{49}/_{288} = 0.170$	0.195
f_{rrrr}				$^{35}/_{288} = 0.122$	0.137
$4f_{\mathrm{mm}}f_{\mathrm{rr}}/f_{\mathrm{mr}}^{2}$		0.889	0.826	0.803	0.750
$\rho = 2f_{\mathrm{m}}f_{\mathrm{r}}/f_{\mathrm{mr}}$		0.972	0.962	0.957	0.937
$\Omega = f_{\mathrm{r}}f_{\mathrm{rrr}}/f_{\mathrm{rr}}^{2}$			0.647	0.648	0.604
$f_{\mathrm{mm}}f_{\mathrm{mmmm}}/f_{\mathrm{mmm}}^{2}$				1.097	0.960
		$\eta = 2, \tau^* = ^{1}/_{4}$			
f_{m}	$^{4}/_{9} = 0.444$	0.467	0.471	0.473	0.480
f_{mm}		$^{1}/_{5} = 0.200$	0.213	0.217	0.224
f_{mr}		$^{8}/_{15} = 0.533$	0.520	0.517	0.512
f_{rr}		$^{4}/_{15} = 0.267$	0.267	0.266	0.264
f_{mmm}			$^{4}/_{45} = 0.089$	0.096	0.102
f_{mmr}			$^{56}/_{225} = 0.249$	0.245	0.243
f_{mrm}			$^{29}/_{225} = 0.129$	0.128	0.128
f_{mrr}			$^{56}/_{225} = 0.249$	0.253	0.256
f_{rmr}			$^{32}/_{225} = 0.142$	0.139	0.134
f_{rrr}			$^{32}/_{225} = 0.142$	0.139	0.136

Table III (*Continued*)

	x				
	2	3	4	5	∞
f_{mmmm}				$^{44}/_{1125} = 0.039$	0.046
f_{mmmr}				$^{128}/_{1125} = 0.114$	0.113
f_{mmrm}				$^{136}/_{1125} = 0.121$	0.123
f_{mmrr}				$^{128}/_{1125} = 0.114$	0.120
f_{mrmr}				$^{152}/_{1125} = 0.135$	0.133
f_{rmmr}				$^{16}/_{225} = 0.071$	0.065
f_{mrrm}				$^{13}/_{225} = 0.058$	0.061
f_{mrrr}				$^{152}/_{1125} = 0.135$	0.133
f_{rmrr}				$^{32}/_{225} = 0.142$	0.136
f_{rrrr}				$^{16}/_{225} = 0.071$	0.069
$4f_{\mathrm{mm}}f_{\mathrm{rr}}/f_{\mathrm{mr}}^2$		0.750	0.842	0.862	0.902
$\rho = 2f_{\mathrm{m}}f_{\mathrm{r}}/f_{\mathrm{mr}}$		0.933	0.958	0.964	0.975
$\Omega = f_{\mathrm{r}}f_{\mathrm{rrr}}/f_{\mathrm{rr}}^2$			0.942	0.929	0.936
$f_{\mathrm{mm}}f_{\mathrm{mmmm}}/f_{\mathrm{mmm}}^2$				0.920	0.984

where k is either m or r for each matrix $\mathbf{U}_{\mathrm{k}}^{(2)}$. The terminating factors are the "vectors"

$$\mathbf{U}_0 = [1 \quad 0 \quad \ldots \quad 0] \qquad \mathbf{U}_x = \mathrm{col}\,(1 \quad 1 \quad \ldots \quad 1) \tag{7}$$

At stereochemical equilibrium the frequency of occurrence of a diastereomer is given by the ratio between Z and the *sum of the conformational partition functions of all chains of the same length, Z.* This sum is given by[2]

$$Z = \mathbf{U}_0 \boldsymbol{U}^{x-1} \mathbf{U}_x \tag{8}$$

where

$$\boldsymbol{U} = \mathbf{U}_{\mathrm{m}}^{(2)} + \mathbf{U}_{\mathrm{r}}^{(2)} \tag{9}$$

The fraction of a stereochemical sequence q of length m at stereochemical equilibrium, averaged over the entire length of the chain of length x, shall be called $f_q(x)$ (e.g., $f_{\mathrm{mrmm}}(x)$ indicates a specific pentad, $m = 5$). The general expression for the fractions of sequences of any length $3 \le m \le x$ may be written as

$$f_q = Z^{-1}(x - m + 1)^{-1}[\mathbf{U}_0\mathbf{0}][\boldsymbol{W}_1{}^{(m-2)}\mathbf{0}]\hat{\boldsymbol{W}}_q{}^{x-m-1}\begin{bmatrix} 0 \\ \cdot \\ \cdot \\ \cdot \\ 0 \\ \mathbf{U}_x \\ \cdot \\ \cdot \\ \cdot \\ \mathbf{U}_x \end{bmatrix} \tag{10}$$

where the supermatrix $\boldsymbol{W}$ is given by

$$\boldsymbol{W} = \begin{bmatrix} 1 \\ 1 \end{bmatrix} \otimes \mathbf{E}_{m-2} \otimes [\mathbf{U}_{\mathrm{m}}^{(2)} \ \mathbf{U}_{\mathrm{r}}^{(2)}] \tag{11}$$

This matrix is of the order $2^{m-2}\nu \times 2^{m-2}\nu$, where ν represents the number of rotational states per main chain bond (in eq 2–4, for example, $\nu = 3$). $\mathbf{E}_{m-2}$ is the unit matrix of order $m - 2$; $\otimes$ indicates the direct product (Kronecker product).[20] $\hat{\boldsymbol{W}}_q$ in turn is given by

$$\hat{\boldsymbol{W}}_q = \begin{bmatrix} \boldsymbol{W} & \boldsymbol{W}'_q \\ \mathbf{0} & \boldsymbol{W} \end{bmatrix} \tag{12}$$

where $\boldsymbol{W}'_q$ is a modification of $\boldsymbol{W}$, determined by q (an incorrect but informative statement is $\boldsymbol{W}'_q = \partial \boldsymbol{W}/\partial q$). The superscript in parentheses in eq 10 indicates the serial product of $m - 2$ matrices $\boldsymbol{W}$, starting with $\boldsymbol{W}_1$.

$\boldsymbol{W}'_q$ may be found by the following algorithm, which is based on the structure of $\boldsymbol{W}$ as defined in eq 11. First, we rewrite q as a number in binary form, replacing m by 0 and r by 1, and call this number ψ (e.g., if q is rmrm, $\psi = 1010_{(2)} = 10_{(10)}$). Then, two natural numbers, g_{R} and g_{C}, are defined by

$$g_{\mathrm{R}} = 1 + \{\psi/2\} \tag{13}$$

$$g_{\mathrm{C}} = 1 + (\psi \text{ modulo } 2^{m-2}) \tag{14}$$

where { } denote the largest natural number not exceeding the quantity enclosed by them, and a modulo $b \equiv a - b\{a/b\}$ is the remainder of a after division by b.

Define the matrices

$$\mathbf{V}_{\mathrm{R}} = \mathrm{diag}\,(\delta_{ig_{\mathrm{R}}}) \equiv [\delta_{ij}\delta_{ig_{\mathrm{R}}}] \tag{15}$$

$$\mathbf{V}_{\mathrm{C}} = \mathrm{diag}\,(\delta_{ig_{\mathrm{C}}}) \equiv [\delta_{ij}\delta_{ig_{\mathrm{C}}}] \tag{16}$$

where δ is the Kronecker delta ($\delta_{kl} = 1$ if $k = l$, $\delta_{kl} = 0$ otherwise). $\mathbf{V}_{\mathrm{R}}$ and $\mathbf{V}_{\mathrm{C}}$ are of order $2^{m-2} \times 2^{m-2}$; all their elements are zero except for the g_{R}th and g_{C}th element on the main diagonal which are unity. $\boldsymbol{W}'_q$ is now given by

$$\boldsymbol{W}'_q = (\mathbf{V}_{\mathrm{R}} \otimes \mathbf{E}_\nu)\boldsymbol{W}(\mathbf{V}_{\mathrm{C}} \otimes \mathbf{E}_\nu) \tag{17}$$

where $\mathbf{E}_\nu$ is the unit matrix of the same order ν as $\mathbf{U}_{\mathrm{m}}^{(2)}$ and $\mathbf{U}_{\mathrm{r}}^{(2)}$. For m-ads that implicitly comprise two different stereosequences the two different matrices $\boldsymbol{W}'_q$ obtained from eq 17 for each sequence must be added (e.g., if q is mmmr, $\boldsymbol{W}'_q$ is the sum of the two matrices formed by eq 17 with mmmr and rmmm). For $m = 3$ eq 10 reduces to Flory's formulation.[2]

Calculation of dyad frequencies, $m = 2$, requires a minor revision of eq 10. The factor $[\boldsymbol{W}_1{}^{(m-2)}\mathbf{0}]$ has to be omitted, and col $(\mathbf{0},\ldots,\mathbf{0},\mathbf{U}_x,\ldots,\mathbf{U}_x)$ has to be replaced by col $(\mathbf{0},\mathbf{U}_x)$, so that

$$f_{\mathrm{m}} = Z^{-1}(x - 1)^{-1}[\mathbf{U}_0\mathbf{0}]\hat{\boldsymbol{W}}_1{}^{(x-1)}\begin{bmatrix} \mathbf{0} \\ \mathbf{U}_x \end{bmatrix} \tag{18}$$

where

$$\boldsymbol{W} = \boldsymbol{U} \tag{19}$$

and

$$\boldsymbol{W}'_{\mathrm{m}} = \mathbf{U}_{\mathrm{m}}^{(2)} \tag{20}$$

This is exactly Flory's result.[2]

All matrices $\boldsymbol{W}'_q$ for $m = 3$, 4, and 5 are given in Table II. The formulation is, however, only limited by the size of the matrices required. The largest matrix, $\hat{\boldsymbol{W}}_q$, is of the order $2^{m-1}\nu \times 2^{m-1}\nu$ (for the usual three-state scheme and pentads, the order of $\hat{\boldsymbol{W}}_q$ is 48 × 48); this is a size easily handled by modern computers for all problems presently anticipated. The procedure presented here also has the practical advantage that it can easily be programmed in general form.

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Numerical Results

Numerical results for three sets of statistical weight parameters are presented in Table III. These sets are the ones arbitrarily chosen in Flory's original work,[2] and they use the matrices in eq 2–4 with $\omega = 0$; i.e., the order of the **U** matrices is reduced to 2×2. For given sequence lengths m, the solution for the smallest chain length $x = m$ was computed by hand and is exact, solutions for longer chains were obtained by numerical methods, and values for infinite chains were obtained by successive squaring of $\hat{W}_q$. Values for $m = 2$ and 3 are identical with Flory's results.[2]

In general, the conformational partition function of a chain as a whole cannot be factorized into separate contributions from independent substructures.[18] This precludes adherence to any type of unidirectional statistics, e.g., of the Markoffian type, although a Bernoullian dyad distribution could be observed in the limit. Deviation of dyad distribution from these common statistics is demonstrated in Table III with the values of quantities often used in testing for given statistics. Testing for Bernoullian statistics is done with[21]

$$4 f_{mm} f_{rr} / f_{mr}^2 \tag{21}$$

and with the *persistence ratio*, ρ[22]

$$\rho = 2 f_m f_r / f_{mr} \tag{22}$$

where both quantities assume values of unity for Bernoullian dyad distributions. Compliance with a first-order Markoff scheme is checked with Ω[23]

$$\Omega = f_r f_{rrr} / f_{rr}^2 \tag{23}$$

that is unity for Bernoullian and first-order Markoffian statistics. Finally we tabulate values for a quantity

$$f_{mm} f_{mmmm} / f_{mmm}^2 \tag{24}$$

that is unity for Bernoullian and first-order and second-order Markoffian dyad distributions.[21] As is obvious from the numbers in Table III, none of these statistics is appropriate for the description of dyad distribution in vinyl chains at stereochemical equilibrium; the numbers approach unity close enough, however, to make experimental proof of the deviation from these types of statistics only possible in exceptional cases.

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Epimerization of Vinyl Polymers to Stereochemical Equilibrium. 2. Polypropylene[1]

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ABSTRACT: Isotactic polypropylene was epimerized to stereochemical equilibrium at 270 °C in the melt under a hydrogen atmosphere, using metallic palladium as catalyst. Equilibrium was reached practically without side reactions. The equilibrium frequencies of the various diastereomeric structures comprising five monomeric units (pentads) were measured by ^{13}C NMR spectroscopy and they were found to agree well with predictions based on a rotational isomeric state model with five states per main chain bond. Other investigated properties of the equilibrate are practically identical with those of so-called "atactic" polypropylene. ^{13}C spin–lattice relaxation times (T_1) were measured for all resolved lines in the spectrum. Relaxation times for the methyl pentad signals mmmm and rrrr were compared with the times obtained in isotactic and predominantly syndiotactic samples and were found to be different in the equilibrate and the stereoregular chains. Schilling and Tonelli's as well as Zambelli et al.'s hexad assignments for the methylene carbon bands were both found to agree reasonably well with the spectrum of the equilibrate.

Introduction

To date, polypropylene is the only vinyl polymer whose stereostructure can be experimentally determined unambiguously in terms of completely assigned pentads[2] and which, at the same time, can be epimerized apparently without side reactions.[3,4] For model compounds equilibrium epimerization has been reported.[5] A detailed conformational analysis has been carried out for this polymer.[6]

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