Polymer Bulletin 24, 305–308 (1990)

Polymer Bulletin

An absolute measure for stereoblock and heterotactic polymers

Ishrat M. Khan

Department of Chemistry, Clark Atlanta University, Atlanta, GA 30314, USA

Summary. A criterion (δ) for testing stereoblock and heterotactic polymers is developed. The criterion takes values between 1 and -1, a value of 1 is indicative of a pure stereoblock polymer and a value of -1 indicates a pure heterotactic polymer. The criterion (δ) is compared with persistence ratio (ρ) and average stereochemical sequence length. The importance of δ as an aid in the synthesis of stereoblock polymers is discussed.

INTRODUCTION

It is of considerable interest to synthesize pure stereoblock and pure heterotactic polymers (1, 2). In a pure stereoblock polymer, an isotactic block (mm...mm) is covalently connected to a syndiotactic block (rr..rr)

mmmmm...mmmmmmrrrrrrr...rrrrr

and in a pure heterotactic polymer, only the mr triad is present. Currently, an absolute criterion for testing the goodness of a stereoblock polymer is not available.

rmrmrmrmrmrmrm...mrmrmrmrmrmrm

In this communication, a criterion (δ) for testing such polymers is developed and the importance of δ in the synthesis of stereoblock and heterotactic polymers is discussed.

DISCUSSION

The criterion (δ), requiring triad stereochemical information is given by the following relationship:

$$\delta = \frac{mm-m^2}{m-m^2} = \frac{rr-r^2}{r-r^2} \approx 1 \qquad (1)$$

That the value of δ should be very close to 1 for a pure stereoblock polymer may be intuitively obvious and can also be demonstrated in the following manner. Using the necessary stereochemical relationship m = mm + 1/2mr (2) we have

$$\frac{mm-m^2}{m-m^2} = \frac{(m-1/2\ mr)-m^2}{m-m^2} \qquad (2)$$

and

$$m \approx mm \qquad (3)$$

because for a high molecular weight pure stereoblock polymer the single heterotactic triad becomes insignificant. Therefore,

$$\frac{mm-m^2}{m-m^2} \approx \frac{m-m^2}{m-m^2} = 1 \qquad (4)$$

Similarly

$$\frac{rr-r^2}{r-r^2} \approx 1 \qquad (5)$$

As an illustration, the criterion can be applied to a theoretically pure stereoblock polymer composed of fifty meso and fifty racemic units, and with only one heterotactic triad. The polymer will have the following dyad and triad contents:

Dyads	Triads
m = .500	mm = .495
r = .500	rr = .495
	mr = .010

Here the necessary stereochemical relationships m = mm + 1/2mr and r = rr + 1/2mr hold (2). A value of δ =.98 is obtained for this polymer which is indicative of a pure stereoblock. In Table I, four theoretically pure polymers,

TABLE I. Tacticity, δ and ρ of Theoretically Pure Polymers

Pol.#	Poly. Type	m	r	mm	mr	rr	δ	ρ
I	Stereoblock	.500	.500	.495	.495	.010	.98	50
II	Stereoblock	.700	.300	.695	.295	.010	.98	41
III	Heterotactic	.500	.500	.000	.000	1.00	-1	0.5
IV	Atactic	.500	.500	.250	.500	.250	0	1.0

in a stereochemical sense, are listed along with the persistence ratios [ρ=2(m)(r)/(mr)] and the values for δ. For polymers I and II, the persistence ratio is a function of the length of the block while in both cases δ is very close to 1, indicating pure stereoblock polymers. The pure heterotactic polymer has a δ value of -1; this may be intuitively clear as such polymers do not have isotactic or syndiotactic triads, i.e. mm = rr = 0. Also, this observation can be demonstrated by taking into consideration that for a pure heterotactic polymer, the following relationship holds:

$$\frac{mm-m^2}{m-m^2} = \frac{-m^2}{m-m^2} \qquad (6)$$

And taking into account that for a pure heterotactic polymer, the number of m and r dyads are equal and from the necessary stereochemical relationship 1-m = r = m, we have

$$\frac{-m^2}{m-m^2} = \frac{-m}{1-m} = \frac{-m}{m} = -1 \qquad (7)$$

Thus, δ is a scale between 1 and -1 and a measure of the goodness of stereoblock and hetereotactic polymers.

In Table II, six polymers with interesting stereochemical characteristics are listed. The average meso sequence length (Z) is calculated as Z = m/.5 (mr) (3).

TABLE II. Tacticity, δ, ρ and Z of Some Stereochemically Interesting Polymers

#	Name[1]	m	r	mm	mr	rr	δ	ρ	Z	Ref.
V	PMMA	.495	.505	.440	.110	.450	.78	4.5	9.0	1
VI	PMMA	.570	.430	.510	.120	.370	.76	4.1	9.5	1
VII	PMMA	.405	.595	.330	.150	.520	.69	3.2	5.4	1
VIII	PMMA	.444	.556	.311	.267	.422	.46	1.9	3.3	4
IX	PMEA	.580	.420	.490	.180	.330	.63	2.7	6.4	5
X	3M2VP	.610	.390	.430	.350	.220	.24	1.4	3.5	6

1) PMMA: Poly(methyl methacrylate)
PMEA: Poly(methyl-α-ethylacrylate)
3M2VP: Poly(3-methyl-2-vinylpyridine)

Polymers V-VII were prepared using synthetic strategies such that only stereoblock polymers were obtained (1) and polymers VIII-X represent ones with reasonably large persistence ratios. From Table II, it is clear that δ is a better measure than ρ and Z of the goodness of stereoblock polymers. Polymers V-VII with values between .69 and .78 are by far the best stereoblock polymers reported in the literature. The fact that ρ does not have an upper limit makes it a poor indicator to quantify the goodness of any stereoblock polymer. Also, polymers I and II, see Table 1, are pure stereoblock polymers with different persistence ratios, this is because ρ depends on the m and r content of the polymers. The average stereochemical sequence length is a poor test of the goodness of stereoblock polymers (see polymers VII and IX), the polymer with the smaller Z has larger values of δ and ρ. Also, the average meso and racemic sequence lengths will in most instances have different values.

The criterion (δ) for testing stereoblock polymers is an absolute one and will prove particularly valuable in the synthesis of stereoblock polymers. This can be accomplished by varying only one of the synthetic conditions (e.g. temperature, solvent system, pressure, counterion in living polymerization) used to prepare the polymer and determining the resulting value for ρ. Depending on whether the value moves closer to or further away from 1.0 will give indication as to the success of the newly implemented conditions. Thus, small changes in the value of δ may be used to monitor progress in the synthesis of stereoblock and hetereotactic polymers.

Acknowledgement. The author gratefully acknowledges partial support of this work by United States Army Research Office Grant # DAAL03-89-G-0087. The author also acknowledge the assistance of Ruby Wright (manuscript secretary, RCMI program, NIH Grant RR03062) in preparation of this manuscript for publication.

References

1. a) M.A. Doherty, T.E. Hogen-Esch, Polymer Preprints, 25(2), 5 (1984); b) M.A. Doherty, T.E. Hogen-Esch, Makromol. Chem., 187, 61 (1986).
2. F.A. Bovey, High Resolution NMR of Macromolecules, Academic, NY (1972).
3. J.C. Randall, E.T. Hsieh, NMR and Macromolecules, ACS Symposium Series, 247, 131 (1984).
4. R.C. Subramanian, R.D. Allen, J.E. McGrath, T.C. Ward, Polymer Preprints, 26(2), 238 (1985).
5. K. Seki, D.A. Tirrell, Polymer Preprints, 24(2), 29 (1983).
6. I.M. Khan, T.E. Hogen-Esch, Macromolecules, 20, 2335 (1987).

Accepted July 17, 1990