blends and of blends of PVC and CPE of identical chlorine content is less surprising. On the other hand, the statistical distribution of comonomer segments in CPE must lead to sufficient microstructural similarity to CPB such that some miscibility occurs. This is reasonable in CPEs of moderate to high chlorine contents where the number of –AA– and –BB– sequences is significant. The phase behavior of the blends examined apparently depends not on the overall mean field interactions but upon those associated with local comonomer sequence distributions.

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Registry No. PVC, 9002-86-2.

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Distribution of Chain Ends inside the Polybutadiene Microspheres of SB Diblock Copolymers

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ABSTRACT: Two polystyrene–polybutadiene block copolymers were examined in small-angle neutron scattering (SANS) experiments designed to probe the location of the polybutadiene chain ends inside the polybutadiene microspheres of these specimens. One of the copolymers, SBm, was phase-matched; the B moiety was synthesized by using a suitable mixture of deuterio and normal butadiene monomer. The other copolymer, SBmBd, contained short perdeuteriated polybutadiene sequences at the end of the polybutadiene block of each of the molecules. Consideration of scattering intensities and the form of the scattering pattern exhibited by SBmBd indicated that the Bd chain ends are essentially uniformly distributed throughout the volume of the spheres. A model in which the Bd ends cluster at the core of the spheres failed to reproduce the essential features of the observed SANS pattern.

Introduction

Diblock copolymers of polystyrene (S) and polybutadiene (B) which display a bulk morphology of B spheres in S matrix have been examined at various levels of structural detail in our laboratory. Among the important features characterized in our previous work using small-angle neutron scattering (SANS) experiments were the BCC packing of the microspheres,[1] the relationship of sphere size to B molecular weight,[2,3] the nature of the interfacial zones between the B spheres and the S matrix,[2] and the effective radius of gyration of the B chain segments of the diblock copolymer.[4,5] Recently we reported on the distribution of S homopolymer added to the S matrix of the diblock.[6]

In this paper we address the following question: Where are the ends of the B chain segments located inside the microspheres? Two possible answers to this question are (a) the ends are essentially uniformly distributed throughout the B spheres and (b) the polybutadiene chain ends are preferentially clustered toward the center of each sphere. Figure 1 demonstrates that it should be relatively easy to discriminate between these two first-order hypotheses if an appropriate pair of diblock copolymers were available for SANS experiments. The necessary pair of copolymers is a phase-matched[7] diblock copolymer, SBm, and a triblock copolymer, SBmBd, in which the first two blocks S and Bm are identical with the phase-matched diblock, and the third, very short end block, Bd, is a perdeuteriated moiety. In the phase-matched diblock the polybutadiene block, Bm, is a random copolymer consisting of an isotopic mixture of protio- and perdeuteriobutadiene repeat units, the ratio of which is carefully selected[7,8] to exactly match the neutron scattering length density of polystyrene. This ideal diblock produces no structural scattering in a SANS experiment as suggested by Figure 1a. However, the triblock containing the short perdeuteriated end blocks will yield substantial amounts of structual scattering because the phase matching is no longer preserved. The detailed nature of the SANS scattering pattern observed for SBmBd will depend dramatically upon the spatial distribution of the Bd chain ends inside the microspheres; thus SANS experiments can be used to determine whether either part b or part c of Figure 1 is a reasonable representation of the chain end distribution in the SBmBd copolymer.

In what follows we describe the synthesis and molecular characterization of copolymers SBm and SBmBd and the examination of these copolymers using SANS experiments and transmission electron microscopy (TEM). Results of

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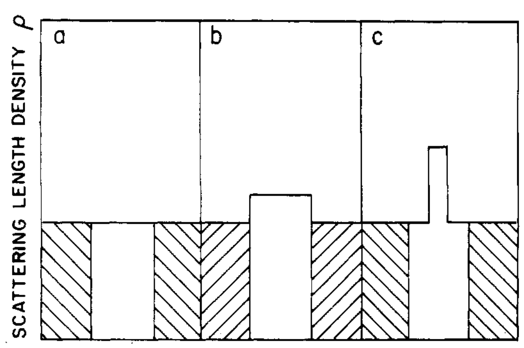

Figure 1. Scattering length density profiles for (a) SBm, (b) SBmBd assuming uniform distribution of Bd ends in the polybutadiene sphere, and (c) SBmBd assuming that the Bd chain ends cluster at the core of the sphere. Polystyrene matrix is crosshatched, and polybutadiene sphere is unshaded.

small-angle X-ray scattering (SAXS) experiments, which are described in detail elsewhere,[8] are also used to support the main conclusions drawn from SANS and TEM results.

Experimental Section

Polymer Synthesis.[8] High vacuum anoinic polymerization techniques, similar to those reviewed by Morton and Fetters,[9] were employed in the synthesis of the block copolymers. A three-stage Kontes/Martin silicone oil diffusion pump facilitated vacuum conditions in the range of 10^{-5} Torr in the primary manifold.

Benzene was stored over fresh, concentrated sulfuric acid (3/1 volume ratio of benzene/acid) for several months during which time the bottom acid layer gradually turned dark brown, indicating that some polar impurities had been oxidized. Acid-treated benzene was washed twice with distilled water, neutralized by washing the dilute sodium bicarbonate solution followed by two washings with distilled water, and finally dried over anhydrous magnesium sulfate. The benzene was further dried by calcium hydride and the addition of a sodium dispersion. The appearance of silvery flecks of sodium indicated that the benzene was dry. It was then distilled on the vacuum line into a storage flask containing poly(styryl)lithium (PS–Li). The retention of the orange-red color of the polystyryl anion indicated that the solvent contained no impurities which would terminate living polymer chains.

Styrene was stirred on the vacuum line with a slurry of ground calcium hydride for several days with periodic degassing. The styrene was then distilled into a flask containing 5 mL of dibutylmagnesium (73 wt % in heptane) and stirred for several hours at room temperature: the solution turned bright yellow as the result of chain initiation by the dibutylmagnesium. The styrene was then degassed, vacuum distilled into calibrated ampules, and diluted with benzene. The ampules, equipped with break seals for attachment to polymerization reactors, were stored in a freezer. The density for styrene monomer at room temperature under its own vapor pressure was determined to be 0.897 g/mL by using a calibrated ampule.

1,3-Butadiene was stirred over lithium aluminum hydride (−20 °C), degassed, and distilled onto *sec*-BuLi. After the solution was stirred at −10 °C for 30 min, the butadiene was distilled into a flask containing dibutylmagnesium and stored under vacuum at −20 °C in the freezer. Before the solution was distilled into the delivery ampule, the monomer was further purified over sodium mirrors. The density of 1,3-butadiene at −78 °C under its own vapor pressure was measured as 0.705 g/mL.

1,3-Butadiene-d_6 was obtained from two sources, Merck, Sharp & Dohme Ltd. and Cambridge Isotope Inc. The purification procedure for the perdeuteriated monomer was identical with that of the normal 1,3-butadiene. Halogenated impurities are removed effectively as lithium salts when reacted with *sec*-BuLi. The density of 1,3-butadiene-d_6 was measured as 0.780 g/mL at −78 °C.

Diblocks SBm and SBmBd were synthesized in one reactor,[8] the triblock being formed by extending a portion of the living SBm diblock with a third block of perdeuteriated butadiene. The mixed ("m") block contained 83% normal polybutadiene.[8] Secondary butyllithium initiator was titrated by using techniques developed by Gilman and Cartledge.[10] Polystyrene synthesis proceeded at room temperature in benzene for 8 h; polybutadiene blocks were produced over 24-h periods. The living polymers were terminated at appropriate stages of the synthesis with degassed methanol yielding approximately 1.9 of the polystyrene block, 4.6 g of SBm, and 17.1 g of SBmBd. Total yield for the synthesis was greater than 99%.

Table I
Molecular Characterization of Polymers

sample	M[b](S)	M(Bm)	M(Bd)	microstructure[c] Bm	microstructure[c] Bd
S[a]	83.4	...	...	...	...
SBm	83.4	10.1[d]	...	.../.../10	...
SBmBd	83.4	10.1	1.2[e]	.../.../10	51/44/5

[a] Polystyrene block of the copolymers. [b] kg/mol; $M_w/M_n < 1.1$. [c] cis 1,4/trans 1,4/vinyl; total 1,4 content of Bm = 90%. [d] Random copolymer; degree of polymerization 183 (152 B and 31 Bd). [e] Degree of polymerization 20.

Molecular Characterization.[8] Homopolymers and diblock copolymers were characterized by using size exclusion chromatography, ultraviolet absorption, proton/carbon-13 NMR experiments, and considerations of the overall stoichiometry of the reaction. The waters GPCII apparatus was calibrated with nine polystyrene standards and two polybutadiene standards obtained from American Polymer Standards Corp. Calibration of the Perkin-Elmer 3B UV/vis spectrophotometer at 262 nm was accomplished by using four carefully prepared solutions of polystyrene in 1,4-dioxane; at this wavelength there is no contribution to the UV absorption from polybutadiene, so the styrene content of SB block copolymers is readily obtained. NMR experiments (Bruker WM250) also provided information on the copolymer compositions and on the polybutadiene microstructures.[8] A summary of the results of characterization experiments appears in Table I.

Morphological Characterization. Transmission electron micrographs were obtained on a Phillips 300 electron microscope operated at 80 kV and calibrated against a diffraction grating with 54 864 lines per inch. Samples were stained in a 1 wt % osmium tetraoxide aqueous solution and cut into sections ~300 Å thick by using a LKB ultramicrotome fitted with a freshly prepared glass knife.

Small-angle neutron scattering was performed at the National Bureau of Standards SANS spectrometer. The alignment, calibration, and transmission measurement were performed with the assistance of Dr. Charles C. Han; the NBS instrumentation has been described in detail in the literature.[11,12] The important characteristics of the SANS instruments as used in this work are as follows: wavelength λ = 6 Å; $\Delta\lambda/\lambda$ = 0.25; sample to detector distance 3.6 m. Silica and a PS/PSd 50/50 blend were used as standards in the calibration procedures.[8]

Specimen Preparation. Polymer films were cast on a mylar film in an aluminum cup from a 5 wt % solution in toluene; solutions were passed through a Millipore Millex-SR 0.5-μm filter prior to casting. During the first 24 h of the film forming period at 60 °C, nitrogen was purged through the cup at a flow rate of 0.1–0.2 standard ft^3/h. A subsequent 10-h drying period at 75 °C employed the same nitrogen flow rate.

Films were cut into 1.5 cm × 1.5 cm square pieces with a thickness of ~0.3 mm. An additional drying process under vacuum employed a heating program starting at room temperature and progressing at a rate of 20–30 °C per day up to 120 °C. Then, the films were cooled, cleaned with methanol, stacked between two glass plates held together by a small binder clip, and transferred into the vacuum oven at 120 °C. No appreciable compression of the film stack was observed during this 10-min heating process. Final film thickness was about 2 mm. Before neutron scattering, all the samples were simultaneously heated without the binder clip to 120 °C under vacuum overnight and cooled down at a rate of 10 °C/h.

Results

Transmission electron micrographs of SBm and SBmBd are shown in parts a and b of Figure 2, respectively.

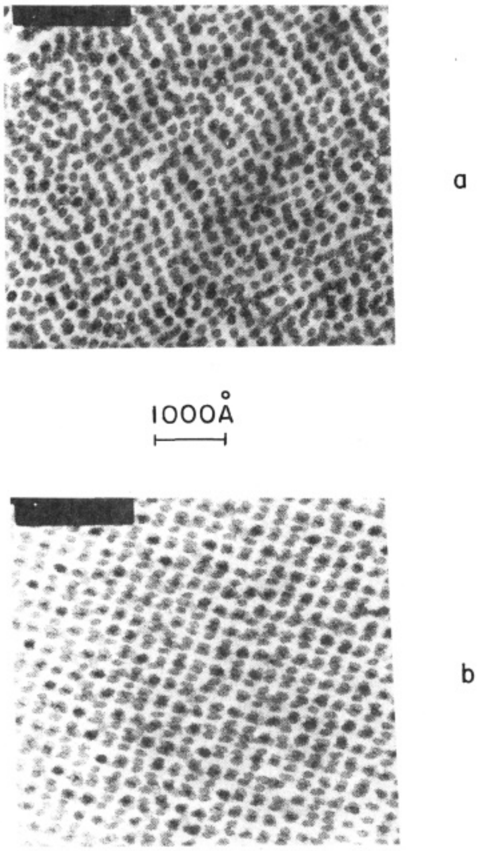

Figure 2. Transmission electron micrographs of osmium tetroxide stained sections of (a) SBm and (b) SBmBd.

Spheres of polybutadiene in a polystyrene matrix are revealed in both photographs. In both cases the sphere diameter is somewhat less than 200 Å.

Results of SANS experiments on SBm and SBmBd appear in parts a and b of Figure 3, respectively. Unlike the micrographs of Figure 2 which are essentially indistinguishable, the SANS patterns for these two samples are strikingly different. For SBm the intensity of scattered neutrons is very close to zero over the entire range of Q ($= 4\pi \sin \theta/\lambda$) covered by the experiment. Intensities for SBmBd are orders of magnitude larger over the same Q range, and significant features are seen in the scattering pattern; a large peak appears near $Q = 0.02$ and a pronounced shoulder appears in the Q range immediately above the peak. Results of SAXS experiments presented elsewhere,[8] covering the same Q range, show exactly the same features seen in SANS (a pronounced peak at the same location as the SANS main peak followed by a higher Q shoulder on this peak); in addition a broad rolling maximum is seen in the SAXS pattern near $Q = 0.06$.

Discussion

We first note that the synthesis of SBm was successful in producing the desired phase-matched[7] result shown schematically in Figure 1a. The featureless scattering pattern with essentially zero intensity (Figure 3a) provides unequivocal evidence that the structural scattering has been eliminated by matching the neutron scattering length densities of the two moieties of the SBm diblock. When the short Bd end blocks are added, thereby producing SBmBd, the structural scattering reappears dramatically (Figure 3b). It is now our task to determine whether or not this reemergent scattering can be used to discriminate between the two extreme cases for Bd chain end distribution mentioned earlier and shown schematically in parts b and c of Figure 1; i.e. we hope to determine from the information contained in Figure 3b whether the Bd chain ends distribute themselves uniformly throughout the polybutadiene spheres or cluster near the centers of the spheres.

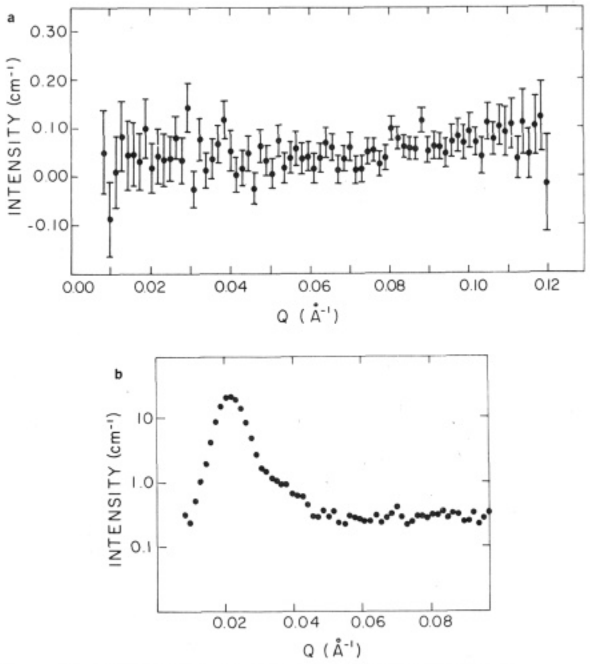

Figure 3. SANS data for (a) SBm and (b) SBmBd.

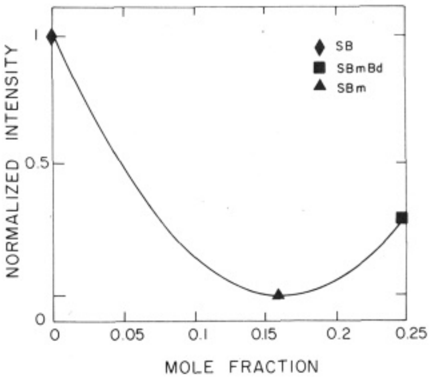

Figure 4. SANS intensity as a function of mole fraction of perdeuteriated repeat units within the polybutadiene spheres assuming uniform distribution of the perdeuteriated material. Solid line: expected behavior based on expressions developed in ref 7 and 13. Data points for samples indicated, normalized to SB intensity.

A first consideration of Figure 3b involves the magnitude of the intensity exhibited by the large peak near $Q = 0.02$. This peak intensity reflects the magnitude of the difference in scattering length density between the polystyrene matrix and the polybutadiene spheres. When this difference is zero the peak intensity is zero as seen in Figure 3a and in our earlier studies[4,5] of composition matched[7] mixtures of two diblocks. Koberstein[7] and Jahshan and Summerfield[13] have developed nearly equivalent expressions which allow for a calculation of the variation of the SANS contrast factor (and therefore scattering intensity) with mole fraction of deuteriated repeat units in the polybutadiene regions of an SB diblock, assuming that these deuteriated units are uniformly distributed within polybutadiene regions. The solid curve of Figure 4 shows this expected variation of intensity with mole fraction of deuteriated B units in a SB block copolymer system. Intensity drops with added deuterio-B units until contrast matching is achieved near 16 mol %. The intensity is expected to rise

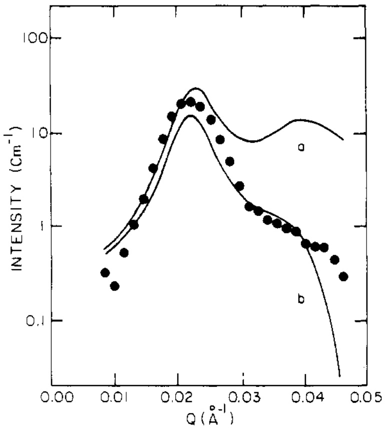

Figure 5. Fits of a combined interparticle interference function and an intraparticle form factor to the SBmBd SANS data. Curve a uses 45 Å for the radius of the intraparticle form factor; curve b, R = 92 Å. Parameters of the interparticle interference function are identical for the two curves.

with further addition of deuteriated B units beyond the point of contrast matching because the scattering length density of the spheres now exceeds that of the polystyrene matrix. The three data points shown in Figure 4 correspond to the normalized scattering intensities (integrated between Q = 0.012 anmd Q = 0.032 Å^{-1}) for three samples: a normal SB diblock[8] with spherical B microdomains for which I_N = 1.0; phase-matched diblock SBm, I_N = 0; and SBmBd, I_N = 0.3. Note that sample SBmBd contains about 25% deuteriopolybutadiene repeat units, 16% from the Bm moiety, and another 9% from the Bd end blocks. The essentially perfect agreement between the observed normalized peak intensity for SBmBd and that expected on the basis of uniform distribution of deuteriated segments in the polybutadiene spheres is strong support for the hypothesis (Figure 1b) of essentially uniform distribution of Bd chain ends in the polybutadiene sphere of SBmBd.

This tentative conclusion is supported by the results of modeling of the form of the scattering pattern exhibited by SBmBd. Previous papers from our laboratory[6] and elsewhere[14] have shown decisively that scattering from block copolymers of spherical morphology can be modeled by an appropriate combination of a Percus–Yevick[15] interparticle interference function and a Bessel function intraparticle form factor. Because the magnitude and distribution of center-to-center distances among spheres do not change when considering either part b or part c of Figure 1, the parameters of the interparticle interference function cannot be expected to discriminate between these two cases. On the other hand, the key parameters of the intraparticle form factor, the effective polybutadiene sphere radius, changes dramatically from part b to part c of Figure 1. For Figure 1b, representing uniformly distributed ends, the appropriate value of the radius of the scattering spheres is the overall radius of the polybutadiene spheres which from TEM (Figure 2b) in known to be about 100 Å and from SAXS data[8] a value of R = 92 Å was determined. In Figure 5, curve b shows the degree to which the SANS data are described by Percus–Yevick interparticle scattering combined with an intraparticle form factor based on a value of 92 Å for the sphere radius. The essential characteristics of the SANS data in this region of Q are described by this model, further supporting the earlier conclusion regarding uniform chain end distribution in the block copolymer spheres. We note further that SAXS and SANS spectra for the case of uniformly distributed ends should be similar, as observed,[8] since both bulk density (SAXS) and neutron scattering length (SANS) vary in the same way throughout the sample. However if chain end clustering occurred, SAXS and SANS spectra would be quite different; the SANS pattern would be dictated by a contrast profile like that of Figure 1c whereas SAXS would still essentially see a profile like that of Figure 1b.

It remains to be shown that the SANS scattering pattern expected for the case of clustered Bd ends (Figure 1c) is significantly different from experimental observations. On the basis of the fact that the Bd segments have about 10% of the Bm chain length, we take the neutron scattering contrast of ~90% of the sphere volume to be matched with polystyrene; the contrast then rises sharply in the inner 10% of each sphere. The radius of this hypothetical perdeuteriated polybutadiene inner sphere is thus about 45 Å. The expected scattering pattern for this case, modeled by using Percus–Yevick parameters as before and an intraparticle form factor with sphere radius of 45 Å, is shown as the solid curve a in Figure 5. Clearly this model does not reproduce the essential features of the observed SANS data. Thus the hypothesis of chain ends clustered at the sphere centers can be rejected.

Summary and Conclusions

A perfectly phase-matched diblock copolymer SBm was suitably fitted with short perdeuteriated end sections (Bd ends of 10% the chain length of Bm) to form a triblock copolymer SBmBd. While TEM micrographs of the copolymers SBm and SBmBd were essentially identical, SANS patterns were remarkably different. The amount of SANS intensity displayed by the SBmBd was consistent with essentially uniform distribution of deuteriated material throughout the polybutadiene spheres. The form of the SANS pattern of SBmBd was very similar to that observed in SAXS experiments; the SANS curve was well described by a Percus–Yevick interparticle interference function and an intraparticle form factor which incorporated the full polybutadiene sphere radius (ca. 92 Å). A similar analysis which incorporated only the inner core of the spheres failed to reproduce the essential features of the SANS data for SBmBd. From these observations it is concluded that the Bd ends of SBmBd are essentially uniformly distributed throughout the polybutadiene spheres and that models which envision the chain ends as being localized at the sphere cores are incorrect.

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Registry No. (S)(Bd)(B) (block copolymer), 115732-62-2; neutron, 12586-31-1.

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A New Look at the "Run Number" Concept in Copolymer Characterization

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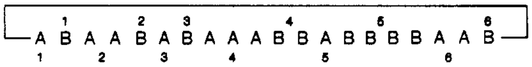
ABSTRACT: The "run number", introduced by Harwood and Ritchey in 1964, is reviewed in this study in light of developments in instrumentation, which now permit run number measurements. The concept is extended to include measurements of "chain punctuation" in semicrystalline polymers, that is, the number of sequences per 100 repeat units that have the capability for crystallization. Intervening sequences, incapable of crystallization, are regarded as chain punctuating units. The "sequence number" is also introduced as an adjunct to the "run number". It is simply the total number of sequences per 100 repeat units of a particular type and includes sequence lengths of one to whatever is the longest sequence length in the copolymer chain.

Introduction

The concept of "run number", which describes the number of times per 100 repeat units a copolymer chain switches from one type of comonomer unit to the other, was introduced by Harwood and Ritchey in 1964.[1] The run number approach to copolymer characterization was developed at a time when it could not be tested because the required experimental data were not available. It was only in the early 1970s with the advent of carbon-13 NMR spectroscopy that *n*-ad distributions in copolymers could be measured and the "run number" concept evaluated. By that time the run number concept was buried deeply in the polymer literature and was essentially waiting to be rediscovered. The first to reexamine the run number was Randall and Hsieh,[2] who demonstrated that observed densities versus run numbers for a series of linear low density polyethylenes gave a single uniform relationship in the 0.920–0.940 density range inspite of differences in branch lengths. The use of "run number" takes into account branches on adjacent repeat units, which allows the number of times the chains are "punctuated" by contiguous units to be determined. The mole percent of comonomer incorporated may or may not reflect the true chain punctuation. It will depend upon the precise manner in which the comonomer repeat units are incorporated. The observed densities in this earlier study were found to be more closely related to the run number than to the overall comonomer contents, which gave a less definitive relationship. The "run number" versus density correlation was also independent of branch length for ethyl, butyl, and hexyl branches.[2] In polymerizations utilizing the classical titanium based Ziegler catalyst system, it is often noted that 1-octene is more efficient than 1-hexene, which, in turn, is more efficient than 1-butene in depressing the density of ethylene–1-olefin copolymers. This hierarchy of efficiency may be related more to a tendency to form both contiguous and alternating 1-olefin derived repeat units, a property resulting from the catalyst used, than to the length of the branch. There may be a small contribution from branch length but it appears to be less significant than the effects from "clustering" and alternation of 1-olefin derived repeat units. Because of the possible new insights gained through the use of the "run number" in copolymer characterization, the run number concept and chain punctuation were explored further in this study.

Harwood and Ritchey defined the "run number" as the percent (AB + BA) diads, which gives the number of A to B plus B to A alternations per 100 copolymer chain units.



In the above sequence,[1] there are 6 "A" runs and 6 "B" runs giving 12 (AB + BA) diads within a sequence of 20 units, which lead to a Harwood and Ritchey "run number" of 60. Note that the ends of the above chain are connected to approximate a long chain, thus precluding the necessity for taking end unit differences into consideration.

In this study, we wish to demonstrate the utility of the "sequence number" when defining chain punctuation. In their original description of "run number", Harwood and Ritchey expressed the total number of times per 100 units an alternation occurred from either A to B or B to A. It may be more meaningful to identify the number of times per 100 repeat units runs of length one or more of a particular type of repeat unit *punctuate* a chain of repeat units of the other type. Note in the above example that the total series of A repeat units is punctuated six times by "B" sequences, and likewise the series of B repeat units is punctuated six times by "A" sequences. The number of "A" sequences must necessarily equal the number of "B" sequences for any copolymer chain that starts with an "A" and ends with a "B" and vice versa. For copolymer chains with like end units, either A or B, the number of "A" sequences will be within plus or minus one of the number of "B" sequences. For high degrees of alternations, the numbers of "A" and "B" sequences, therefore, become essentially the same regardless of whether the end units are alike or different. It is this view of chain punctuation that may be more useful than the "run number", which is

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