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Molecular Factors Affecting the Miscibility Behavior of Cycloolefin Copolymers

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ABSTRACT: The mutual miscibility diagram is determined for binary blends of two ethylene/norbornene random copolymers, and their monomer sequence distribution is investigated by ^{13}C NMR spectroscopy. The miscibility changes abruptly at a norbornene content of 50% where NMR measurements indicate a change in microstructure. When both copolymers have a norbornene content higher than 50%, all blends are miscible within the composition ranges available. A simplified version of the lattice cluster theory (LCT) is applied to this system. The computations indicate that the chain stiffness (arising from the rigidity and steric interactions of the norbornene units) exerts significant influence on the miscibility of these blends. Experimental miscibility diagrams agree reasonably with the LCT predictions.

Introduction

There is considerable technological interest in developing miscible polymer blends since they may have properties intermediate between those of the pure components or may exhibit synergistic effects where the properties of the blend are superior to those of either constituent separately. In this context, blending a copolymer A_xB_{1-x} with other constituents often may be used to enhance miscibility. Indeed, the extension of classic Flory−Huggins theory[1,2] to random copolymers[3,4] shows that sufficiently repulsive A−B interactions may promote the miscibility of the A_xB_{1-x}/C blend. For instance, there is a certain range of compositions for which copolymers of styrene and acrylonitrile are miscible with poly(methyl methacrylate), whereas polystyrene and polyacrylonitrile are both immiscible with poly(methyl methacrylate).

Since differences in miscibility are observed between block copolymers, random copolymers, and alternating copolymers having the same chemical composition, another issue in designing copolymer blends involves evaluating how copolymer microstructure affects the miscibility. This point is heightened by the recent progress in metallocene catalysis that allows the control of molecular architecture. For example, the monomer sequence distribution of cycloolefin copolymers[5−7] can be designed by the selected use of catalyst systems.[8,9]

In the present work, we determine the mutual miscibility diagram of ethylene/norbornene copolymers and investigate their microstructure. This system is interesting because of the presence of cyclic olefins in the chain backbone and because of the large size and stiffness disparities between the ethylene and norbornene monomers. The experimental data are compared with theoretical analysis in order to determine how the size and stiffness disparities and monomer sequence distribution affect the miscibility patterns.

Table 1. List of Copolymers and Their Main Characteristics

polymer	norbornene content (%)	T_g (°C)[a]	M_w[b]	polydispersity[b]
1	36.1	76	103 080	2.89
2	48.8	132	90 890	2.21
3	54.3	139	74 126	2.49
4	58.1	152	97 640	2.39
5	63	176	100 220	2.26
6	74.2	203	74 830	2.7
7	76.1	218	77 430	2.85

[a] According to ref 5. [b] Relative to a polystyrene standard.

Experimental Methods and Results

Materials. Copolymers of ethylene and norbornene have been provided by Hoechst Celanese and have been synthesized using metallocene catalysis.[5−7] Table 1 describes the main characteristics of these copolymers as a function of the norbornene content.

Sequence Distribution. The compositional distribution along the chain has been investigated by NMR spectroscopy. NMR spectra are obtained using a Bruker AMX 500 spectrometer operating at 125.77 MHz for ^{13}C with 10 mm diameter sample tubes for maximum signal-to-noise. $CDCl_3$ is used as solvent, lock, and reference (77.0 ppm vs tetramethylsilane). Carbon spectra are obtained with the minimal nuclear Overhauser effect by decoupling only during the 0.5 s acquisition time with a 5 s recycle delay and 30° carbon pulses. The data acquisition generally requires several hours to overnight.

Figure 1 displays the NMR spectra obtained for different copolymer compositions. As noted previously,[8] as the composition varies, the chemical structure of the cycloolefin copolymers differs. Rische et al.[10] divide spectra into two distinct patterns depending on the norbornene content. For low norbornene content (less than 50%), the resonances are relatively well separated, whereas signal groups are broader and less well separated when the norbornene content is higher than 50%.

Because norbornene contributes two originally equivalent C2/C3 carbons (see Table 2) to the backbone of the copolymer, the usual notation for compositional sequences along the chain is not sufficient: the two norbornene main-chain carbons become inequivalent when the monomer identities differ on either side of a given norbornene monomer. As discussed below, to the level of our observations, we find that the main contributors to the observed chemical shifts are the sequences

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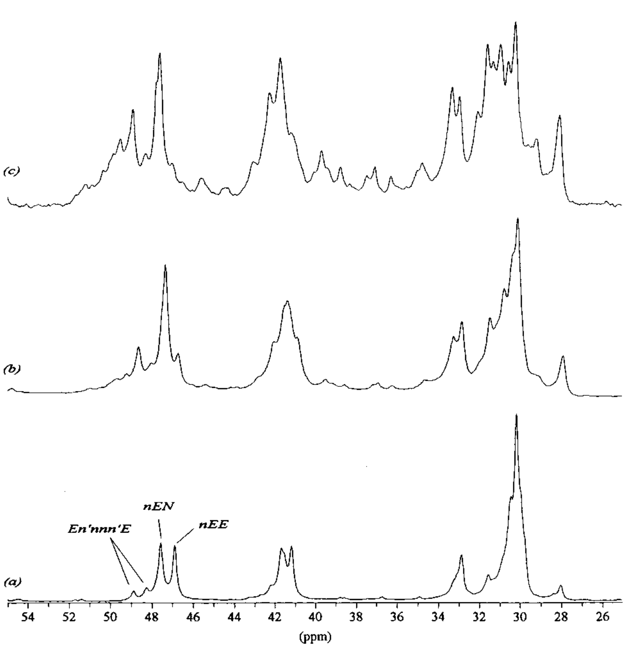
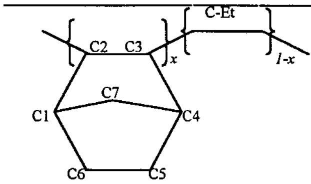


Figure 1. Example of ^{13}C NMR spectra of ethylene−norbornene copolymers with norbornene contents of (a) 36.1%, (b) 54.3%, and (c) 74.2%.

Table 2. NMR Assignments

Copolymer Structure	Shift (ppm)	Assignment
	27.8-30.0	C-Et
	30.1-32.0	C5/C6 methylene
	32.0-33	C7 methylene
	40.5-42.5	C1/C4 methine
	46.5-52.0	C2/C3 methine

along one chain direction from one norbornyl carbon designated as *n*, without reference to the monomer sequence in the other chain direction. Thus, *n* is the backbone carbon we are assigning with respect to the ensuing components along the chain with, of course, no capacity to physically distinguish any directionality. We use the notation such as *nEN* for an alternating copolymer sequence, *nEE* for a norbornyl monomer followed by at least two ethylene monomers, and *En′nnn′E* to note the inequivalent C2/C3 pairs in an *ENNE* sequence.

We first consider the case of low norbornene content (spectrum a in Figure 1). The signals at 46−52 ppm are assigned to the C2/C3 methine group carbons of the norbornene units (see Table 2). Since the C2/C3 carbons connect norbornene monomers to adjacent norbornene or ethylene units in the polymer chain, this region of the spectrum is of particular interest. Four main resonances are observed in this range. The signal at 46.7 ppm is assigned to an *nEE* sequence, whereas the signal at 47.3 ppm corresponds to the same carbons of *nEN* units. The next two resonances at 48.05 and 48.64 ppm arise from norbornene blocks *nN*. A recent investigation of the (norbornene-*co*-ethylene) polymer microstructure[11] gives more details about the length of norbornene blocks. Four cross-peaks were observed and assigned to *nEE*, *nEN*, and *nN* units as the shift is increased, in accordance with our assignments. This latter study also demonstrated that the length of norbornene blocks does not exceed two norbornene units for low norbornene content. Consequently, the two signals observed at 48.05 and 48.64 ppm on spectrum a of Figure 1 can reasonably be assigned to norbornene *En′nnn′E* sequences. Thus, when the norbornene content is low (less than 50%), the polymer chain consists mainly of norbornene units bonded to ethylene units. Norbornene blocks also exist, but their length does not exceed two norbornene units.

We now discuss the samples with high norbornene content. As the norbornene content increases (spectra b and c of Figure 1), the signal groups are broader, and resonances are less well separated. The relative intensities of resonances assigned to *nEE* and *nEN* units decrease, and new resonances appear, probably arising from norbornene blocks whose length exceeds two norbornene units. The shifts appearing around 35−38 ppm correspond to the terminal unit of a norbornene trimer as has been reported in the literature.[12] This last piece of information suggests that the norbornene block length does not exceed three norbornene units, all the more so because even the insertion of three norbornene units in a row has been shown to be improbable.[11] Unlike the situation at low norbornene content, the copolymer chain for high norbornene content reveals more of a block norbornene structure and includes mostly *En′nnn′E*, *NNN*, and *nEN* sequences.

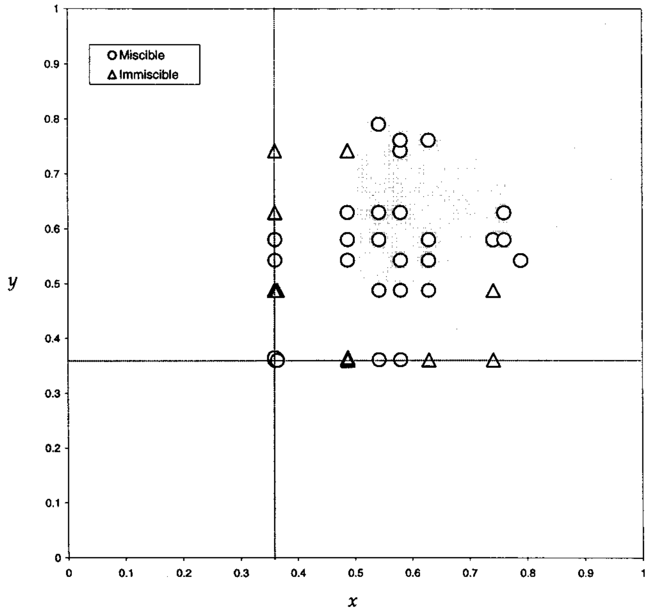


Figure 2. Mutual miscibility data for equal weight fraction binary blends of ethylene/norborene copolymers N_xE_{1-x}/N_yE_{1-y}. The data are insensitive to temperature over the range 250−350 °C. The shaded area indicates the miscibility region for x, $y > 50\%$. Lines correspond to constant compositions x and $y = 36.1\%$ as guides for the eye.

Miscibility Diagram. The mutual miscibility of cycloolefin copolymers has been established by DSC measurements. Inspection of Table 1 shows that as the norbornene content increases, the glass transition temperature T_g varies from 76 to 218 °C. The criterion for miscibility is that a miscible blend exhibits a single T_g, whereas an immiscible blend displays a pair of T_g's. For this purpose, equal weight fraction blends of copolymers of different composition have been prepared by dropwise precipitation from solution (100 mg of each copolymer is dissolved in 10 mL of *m*-xylene) in stirred methanol. Blends are collected as a fine powder and then dried to constant weight in a vacuum oven.

DSC measurements are performed with a Perkin-Elmer DSC 7 in an N_2 atmosphere with sample sizes about 10 mg. All blends are first heated at a rate of 20 °C/min to T_h (T_h varied from 250 to 350 °C), held at T_h for 5 min, and quenched to 0 °C at a rate of 500 °C/min. One T_g is observed for all blends during the first scan. Then, they are scanned from 20 to 250 °C. Depending on the blend constituents, one or two T_g's are observed. Note that whatever the holding temperature T_h, the results remain unchanged. The miscibility only depends on the blend composition in the temperature range investigated.

Figure 2 depicts the experimental miscibility for equal weight fraction blends of the ethylene/norbornene random copolymers. The abscissa *x* represents the norbornene content of copolymer 1 (N_xE_{1-x}), and the ordinate *y* denotes the composition of copolymer 2 (N_yE_{1-y}). Figure 2 shows that the region of miscibility is not governed solely by $|x - y|$ and, therefore, departs strongly from the prediction of random copolymer FH theory (see Discussion). Furthermore, Figure 2 reveals two noteworthy features. First, when both blend constituents have a norbornene content higher than 50% (depicted by the gray background in Figure 2), the blends are miscible over the whole range of copolymer compositions available (with ($|x - y| < 30\%$). Second, the range of miscibility diminishes significantly when x and y are less than 0.5. A particular interesting behavior emerges when x or y is 0.361 (the dotted lines in Figure 2) where multiple miscibility windows appear. Clearly, the miscibility ceases to be governed simply by the magnitude of the composition difference $|x - y|$ as in random copolymer Flory−Huggins theory. Unfortunately, samples are unavailable with norbornene content less than 36%.

Discussion

The simplest model for describing binary random copolymer mixtures is an extension[3,4] of Flory−Huggins (FH) theory to random copolymers. For a blend of two copolymers of the same nature but different compositions, this formalism predicts that the miscibility window exists for $|x - y| < |x - y|_c$ which is independent of the copolymer composition.[13] This contrasts with our results, which exhibit a strong composition dependence. To explain departures from random copolymer FH theory, at least three theories have been proposed. The following sections discuss these three different theoretical approaches.

The Model of Balazs et al.[14] The phenomenological model of Balazs et al. appends a sequence dependence into the random copolymer version of FH theory to explain the observed dependence of the miscibility window parameter $|x - y|_c$ on the copolymer compositions. These authors argue that the interaction parameter χ_{AB} is influenced by the neighboring units, chemically bonded to the A or B monomer. They introduce several interaction parameters, such as $\chi_{\text{triad, triad}}$, to account for the microstructure dependence, where the subscript triad designates a set of three successive monomers. A similar model[15] with explicit sequence distribution has been developed subsequently using slightly different assumptions. It might seem desirable to apply one of these models to our results, especially because our NMR data as well as the mutual miscibility diagram exhibit a strong transition at a norbornene content equal to 50%, which suggests a strong effect of microstructure on the miscibility behavior. Unfortunately, the complexity of the NMR spectra for high norbornene contents currently renders a quantitative determination of the sequence distribution impossible, and thus the numerous interaction parameters of the model cannot be evaluated without introducing additional assumptions.

Solubility Parameter Formalism. A large departure from FH type theories in binary blends of ethylene−butene copolymers and a dependence of the miscibility window parameter $|x - y|_c$ on blend composition have also been observed by Graessley and co-workers.[16] Although the random copolymer theories mentioned above[14,15] have been shown to agree with a large body of experimental data, these authors argue that the physical significance remains unclear for the extra interaction parameters (e.g., the triad−triad interactions) in these models.[14,15] Instead, Graessley et al. analyze their data using the solubility parameter formalism which expresses the interaction parameter in the form $\chi \propto (\delta_1 - \delta_2)^2$, where δ_1 and δ_2 are the solubility parameters for the individual blend components. The solubility parameters deduced from small-angle neutron scattering data have been found to provide good agreement with those deduced from pure component PVT properties. Thus, the observed departure from FH behavior has been related to the nonlinear variation of solubility parameter with copolymer composition. The experiments of Graessley and co-workers also show that differences in the sequence distribution of the ethylene branches in random copolymers exert only a small effect on the solubility parameters.[17] Graessley and co-workers have applied this formalism to several polyolefin blends, finding that 20−30% of the binary polyolefin blends yield anomalous mixing, i.e., strong departures from the solubility parameter model.[17−19]

Solubility parameters for the ethylene−norbornene copolymers have been approximated using van Krevelen's group additivity method,[20] and the blend interaction parameters χ are then estimated by applying the standard solubility formalism. This approximation produces the same overall trend as the experimental results; namely, the miscibility increases with norbornene content. It is not possible to comment on the nature of the mixing as defined by Graessley et al. since pure component PVT properties are not available for these copolymers. Nevertheless, this rough calculation indicates that the observed departure from FH theory does not necessarily arise from mixing anomalies but may be the consequences of nonlinear variations of the pure component PVT properties with chemical microstructure. However, the solubility parameter approach is quite deficient in explaining why, when, and how the solubility parameters vary nonlinearly with microstructure. Moreover, the approximate solubility parameter model based on the use of the internal pressure $(\partial U/\partial V)_T$, in principle, omits the entropic portion of χ which is present for many random copolymer polyolefin blends and which, as shown below, is essential for describing the miscibility patterns exhibited by the ethylene/norbornene random copolymer blends.

Lattice Cluster Theory. Although the solubility parameter formalism has been shown to be suitable for describing roughly 70% of the observed polyolefin mixtures, this method does not explain the occurrence of irregular mixing. The lattice cluster theory (LCT),[21−23] which includes contributions from local correlations and specifies structures for individual monomers, has been successfully applied to explain the molecular origins of anomalous mixing in polyolefin blends. For instance, LCT computations[24] have explained the occurrence of lower critical solution temperature (LCST) phase diagrams and the rather large and negative value of the interaction parameter χ in blends of polyisobutylene with other polyolefins.[25] The LCT has also been used to describe the monomer sequence dependence[26] of χ and the pressure dependence of miscibilities in various copolymer systems.[27] The next sections describe the application of the LCT to ethylene/norbornene copolymers and present a comparison with experimental data.

Monomer Structure and Effective Interactions. Because of the restriction of available LCT derivations[23,28,29] to a cubic lattice and due to the inability of the available theory to describe monomer structures containing closed rings, we use an approximate model to represent the structure of the norbornene monomer. While the chosen structure, depicted in Figure 3, appears to be quite different from that of the real norbornene monomer, it is designed to reflect the overall size and shape of the actual norbornene monomer,

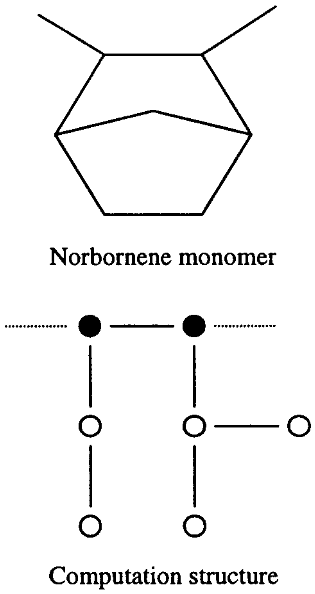


Figure 3. United atom group model of norbornene. Each circle represents a single united atom CH$_n$ (n = 1, 2) group which occupies a single lattice site.

which is the important feature in computing the "entropic" portion of χ. Within the simplified approach described below, the "enthalpic" part of χ is determined solely by one structural property of the monomers, namely, the numbers of united atom groups in the monomers of each species. These numbers are correctly incorporated by the structure in Figure 3 for norbornene and the obvious united atom model for the ethylene units. The norbornene structure in Figure 3 contains seven united atom groups and therefore occupies seven lattice sites ($s_N = 7$), while the ethylene monomer is a two-bead dimer composed of two CH$_2$ groups that cover $s_E = 2$ lattice sites. The site occupancy indices for the single N_xE_{1-x} and N_yE_{1-y} chains respectively are defined as

$$M_1 = s_N n_1^{(N)} + s_E n_1^{(E)}$$

$$M_2 = s_N n_2^{(N)} + s_E n_2^{(E)} \qquad (1)$$

where the average numbers $n_1^{(N)}$ and $n_1^{(E)}$ of norbornene and ethylene monomers in copolymers of species i satisfy the conditions

$$\frac{n_1^{(N)}}{n_1^{(N)} + n_1^{(E)}} = x; \quad \frac{n_2^{(N)}}{n_2^{(N)} + n_2^{(E)}} = y \qquad (2)$$

A simplified version of the LCT is now applied to a binary blend of N_xE_{1-x} and N_yE_{1-y} random copolymers[30] after outlining the basic assumptions of theory. A more detailed description of the theory will be described elsewhere for general A_xB_{1-x}/C_yD_{1-y} random copolymer blends.[30] Within this approach, the enthalpic portion χ_h of the interaction parameter χ is computed by extending FH type (random mixing) counting methods to random copolymers composed of monomers with united atom groups as described above. Thus, χ_h is obtained as

$$\chi_h = \left[\frac{s_N s_E (x-y)}{s_1 s_2}\right]^2 \frac{z\epsilon}{2kT} \qquad (3)$$

where

$$s_1 = s_N x + s_E(1-x) \qquad (3a)$$

$$s_2 = s_N y + s_E(1-y) \qquad (3b)$$

designate the average numbers of united atom groups in the monomers of species 1 and 2, respectively.[31] The χ_h in eq 3 depends only on the compositions x and y and on the numbers (s_N and s_E) of united atom groups in both types of monomers, but not on any other details of the monomer structures as is the case in more sophisticated LCT descriptions that have been derived for binary homopolymer blends.[24,32,33] The lattice coordination number z is taken as $z = 6$, k is Boltzmann's constant, T is the absolute temperature, and $\epsilon = \epsilon_{NN} + \epsilon_{EE} - 2\epsilon_{EN}$ is the exchange energy with ϵ_{NN}, ϵ_{EE}, and ϵ_{EN} denoting the attractive van der Waals energies between united atom groups of the respective monomer pairs, assuming for simplicity that all united atom groups of a given monomer interact with the same energy. The use of united atom interaction energies represents a physically more faithful interaction model than the customary FH approach based on monomer–monomer interaction parameters.[4]

The temperature-independent, "entropic" portion χ_s of χ is generated from the high molecular weight, athermal incompressible limit of the LCT as[24,31]

$$\chi_s = \frac{1}{z^2}\left[\frac{N_2^{(1)}}{M_1} - \frac{N_2^{(2)}}{M_2}\right]^2 = \frac{1}{z^2}\left[\frac{s_N^{\text{tri}} s_E (x-y)}{s_1 s_2}\right]^2 \qquad (4)$$

where $N_2^{(1)}$ and $N_2^{(2)}$ are the numbers of distinct pairs of consecutive bonds in single chains of copolymer species 1 and 2, respectively. The ratios $r_1 = N_2^{(1)}/M_1$ and $r_2 = N_2^{(2)}/M_2$ can be expressed[31,34] more conveniently in terms of the numbers s_α^{tri} and s_α^{tetra} of tri- and tetrafunctional united atom groups in monomers of type α,

$$r_1 = N_2^{(1)}/M_1 = \frac{(s_N + s_N^{\text{tri}})x + s_E(1-x)}{s_N x + s_E(1-x)} = \frac{10x + 2(1-x)}{7x + 2(1-x)}$$

$$r_2 = N_2^{(2)}/M_2 = \frac{(s_N + s_N^{\text{tri}})y + s_E(1-y)}{s_N y + s_E(1-y)} = \frac{10y + 2(1-y)}{7y + 2(1-y)} \qquad (5)$$

Combining the entropic and enthalpic portions yields the blend composition independent χ parameter as

$$\chi = \chi_s + \chi_h = \left[\frac{x-y}{s_1 s_2}\right]^2 \left[\frac{(s_E s_N^{\text{tri}})^2}{z^2} + (s_N s_E)^2 \frac{z\epsilon}{2kT}\right] \qquad (6)$$

which is defined here on a per lattice site (i.e., united atom group) basis. Converting to the more traditional monomer–monomer interaction parameter (for both the SANS χ_{exp} and the χ_{exp} in the free energy) merely involves a multiplicative factor,[24]

$$\chi_{\text{exp}} = \chi\sqrt{s_1 s_2} \qquad (7)$$

where the individual factors of s_1 and s_2 are given by eqs 3a and 3b, respectively.

Note that the above simplified version of the LCT contains but a single adjustable parameter, ϵ. Thus, this LCT approach has the same number of adjustable parameters as in the original extension of FH theory to random copolymers,[3,4] but far fewer than the subsequent extensions[14,15] designed to introduce sequence dependence. Since a solubility parameter model would involve using different (temperature-dependent) solubility parameters for each of the seven samples studied, these models likewise require far more parameters with rather little microscopic interpretation.

The stability condition for a mixture of the two random copolymers may be written as

$$S \equiv \frac{1}{M_1\varphi_1} + \frac{1}{M_2\varphi_2} - 2\chi = 0 \qquad (8)$$

where φ_1 and φ_2 are the volume fractions of both blend components ($\varphi_1 + \varphi_2 = 1$), M_1 and M_2 are site occupancy indices for single chains of these two species as given in eq 1, and the interaction parameter χ is determined from eq 6. Volume fractions $\varphi_1 = 1 - \varphi_2$ and weight fractions $\omega_1 = 1 - \omega_2$ are related by, for instance,

$$\varphi_1 = \frac{2 + 5x}{2 + 5x + \dfrac{(28 + 66x)(1 - w_1)(2 + 5y)}{w_1(28 + 66y)}} \qquad (9)$$

and it is readily verified that the differences between φ_i and w_i are very slight for the norbornene/ethylene copolymer blends because the average united atom group of the norbornene is very similar to the CH_2 groups of the ethylene monomers. The constraint in eq 8 is readily converted to the form of curves $y = y(x)$ that separate the regions of miscibility and immiscibility. For the present case, the equation $y = y(x)$ is a cubic equation which is solved numerically. For comparison, the random copolymer FH theory yields a quadratic equation $y = y(x)$ with the simple solution of two parallel lines $y = x \pm c$, where the constant c for an equal volume fraction blend emerges as $c = [(N_1 + N_2)/(N_1N_2\chi_{AB})]^{1/2}$ and depends only on the polymerization indices N_i (i = 1, 2) and the binary homopolymer blend interaction parameter χ_{AB}.

Equation 6 for χ applies to a model in which all bonds are taken as completely flexible. The rigidity of the norbornene unit may be modeled by taking the two pairs of side group bonds as completely stiff. Introducing this modification into χ_s leads to the alternative model,

$$\chi = \left[\frac{x - y}{s_1s_2}\right]^2\left[\frac{[s_E(s_N^{tri} - 2)]^2}{z^2} + (s_1s_2)^2\frac{z\epsilon}{2kT}\right] \qquad (10)$$

which again contains a single adjustable parameter. We also test a third model that is based on the assumption that adjacent norbornene monomers are connected by semiflexible bonds. The enthalpic portion χ_h remains unchanged from the first two models, whereas χ_s is modified to

$$\chi_s = \frac{1}{z^2}\{[s_N^{tri}s_E(x - y) + 2(g - 1)(s_N - s_E)xy(x - y) + 2(g - 1)s_E(x^2 - y^2)\}/s_1s_2]^2 \qquad (11)$$

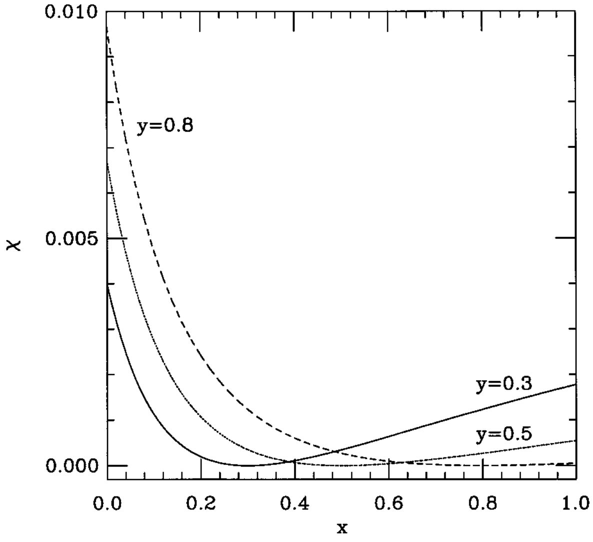


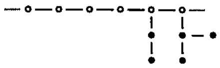
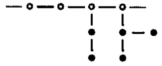
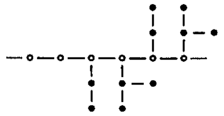
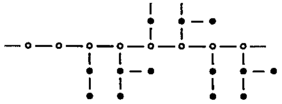
Figure 4. Computed interaction parameter χ for N_xE_{1-x}/N_yE_{1-y} blends [from eq 6] as a function of the composition x for a few compositions y of copolymer 2. The dimensionless exchange energy is chosen as $\epsilon/kT = 0.002$.

where $g = z/[z - 1 + \exp(E_b/kT)]$ and E_b is the trans–gauche energy difference[29] which represents a second adjustable parameter.

Monomer Sequence and the Interaction Parameters. The miscibility data displayed in Figure 2 are independent of temperature over the temperature range 250–350 °C. Note that for copolymer blends with a low norbornene content, which yield T_g at lower temperatures, we have investigated the blend miscibilty using a holding temperature T_h of 150 °C. The results obtained for these blends remain unchanged even over the larger temperature range 150–350 °C. The insensitivity of miscibility data to temperature does not discriminate between either UCST or LCST behavior. (A more detailed experimental description for the nature of the temperature dependence would require a more thorough investigation, for example, by small-angle neutron scattering.) The observed behavior and comparison with theory, however, indicate that the exchange energy ϵ is rather small and positive (indicative of UCST phase diagrams) for this particular system. Hence, the temperature independence of the miscibility patterns suggests that the miscibility is controlled primarily by entropic effects. Figure 4 depicts the interaction parameter χ computed from eq 6 as a function of the copolymer 1 composition x for three different compositions y of copolymer 2 and for the fixed dimensionless exchange energy $\epsilon/kT = 0.002$. The parabolic curves become wider as the norbornene content y of copolymer 2 increases in accordance with our observations that miscibility improves when both x and y are larger.

As mentioned above, the NMR spectra display two distinct patterns as the norbornene content varies. For norbornene content lower than 50%, the copolymer chain includes mostly isolated and alternating norbornene sequences and norbornene dyads. On the contrary, norbornene dyads and triads are predominant in higher norbornene content copolymers. These results clearly demonstrate that copolymers used in this study are not purely random. To estimate the potential effect of sequence distribution on miscibility, we compute the entropic component χ_s of χ for blends of model copolymers with specified monomer sequence. In this case, both blend components are treated as "homopolymers"

Table 3. Monomer Structure and Geometrical Coefficients of Defined Sequence Copolymers

	Monomer Structure	Norbornene Content	Geometrical Coefficient, r_i
α		1/3	14/11
β		1/2	4/3
γ		2/3	11/8
δ		3/4	32/23

with the averaged monomer structures specified in Table 3 which also provides the geometrical coefficients r_i. However, within the simple LCT approximation employed, $\chi_s = (r_1 - r_2)^2/z^2$ turns out to be invariant to the monomer sequence.[31] Consequently, χ_s for an A_xB_{1-x}/A_yB_{1-y} random copolymer blend with given x and y is identical to χ_s for a binary homopolymer blend whose components have a definite alternating sequence of comonomers with the same x and y. This behavior emerges for all cases considered and is readily inferred because the numbers of tri- and tetrafunctional units in the chain are independent of the monomer sequence. Higher-order corrections to the entropic χ_s, which are neglected here, involve terms that depend on monomer sequence.[31]

Side-Group Chain Stiffness. We have already mentioned the inapplicability of the available LCT to monomer structures with closed rings. Moreover, the structure used for the norbornene unit permits more mobility than is expected for a closed ring. Indeed, all calculations based on eq 6 assume complete flexibility of all bonds. To rectify this deficiency and to assess the restriction of mobility imposed by the actual norbornene monomer, computations of χ_s have been performed assuming that the two pairs of side-group bonds of each norbornene monomer are completely rigid (the vertical bond pairs in Figure 3). Of course, this model is still approximate, but it enables quantitatively assessing the influence of the rigidity of the norbornene monomers on χ_s and, hence, on the miscibility. Figure 5a−d displays the entropic component of χ as a function of x (with y fixed) for both the completely flexible and the completely rigid side-group models (solid and dotted lines, respectively) of the copolymer blend. The presence of pairs of completely rigid side-group bonds leads to lower values of χ_s, a result that indicates better miscibility. Moreover, Figure 5a−d also suggests that the improvement in the miscibility should be very significant since the differences in χ_s between the two cases are large.

Backbone Chain Stiffness. Because chain backbone stiffness has been widely considered as a major factor controlling miscibility in athermal blends[35,36] and because the chain stiffness of the ethylene−norbornene copolymers varies as the norbornene content increases due to steric interactions, we include this feature into our analysis (see eq 11) by ascribing a bending energy (i.e., a trans ↔ gauche energy difference) to the backbone bonds connecting adjacent norbornene units,[24] a model with explicit sequence dependence. The geometrical coefficients r_i now depend on temperature and on the bending energy E_b. Figure 5a−d also presents computations of the entropic component χ_s for this semiflexible backbone model of the random copolymer blend (dashed lines). The figures indicate that introducing backbone stiffness also improves miscibility. The influence of chain backbone stiffness is quite notable, especially when the composition difference $|x - y|$ is large.

Quantitative Comparisons between Theory and Experiment. While the analysis of χ_s provides some insight into general trends in the miscibility of norbornene/ethylene copolymers, a quantitative comparison between theoretical predictions and experimental data requires the evaluation of the miscibility diagram $y = y(x)$ for specific values of the exchange energy ϵ. As noted above, we have tested three different models for the norbornene/ethylene copolymers, ranging from a fully flexible chain model to models that include chain stiffness arising within each norbornene unit or from the steric interactions between neighboring norbornene monomers. The latter two models have been found to represent best the experimental data, and illustrative examples are presented in the miscibility diagrams of Figures 6 and 7. (The superiority of these two models is already suggested by Figure 5a−d.) Figure 6 compares the experiment data with calculations assuming rigid bonds within the norbornene monomer, whereas Figure 7 describes the same comparison for the copolymer model with semiflexible backbone bonds for successive norbonene monomers. Squares and crosses in both figures denote the compositions x and y for which the N_xE_{1-x}/N_yE_{1-y} system is computed to be miscible ($S > 0$) and immiscible ($S < 0$), respectively. The fancy squares and crosses indicate the compositions where the miscibility is not predicted correctly and thus where theory disagrees with experiment. There are only four such points (x,y) of disagreement in each figure. However, because the miscibility diagrams are symmetric about the line $x = y$ [i.e., the points (x,y) and (y,x) correspond to *the same system*], the disagreements with experiment emerge for only two samples within each model. Notably, each of the two models fails for different samples, but the overall number of correct predictions is the same in both cases. Figure 8 provides an alternative comparison between the three models by presenting the phase boundaries $y = y(x)$ separating the regions of miscibility and immiscibility for the N_xE_{1-x}/N_yE_{1-y} blends with fixed polymerization indices $N_1 = N_2 = 10^3$ for all x and y. The miscibility window becomes broader when both x and y are large, consistent with the discussion above.

Conclusion

The mutual miscibility of ethylene/norbornene copolymers (denoted as N_xE_{1-x}/N_yE_{1-y}) exhibits large departures from Flory−Huggins type theories which predict that the blends are miscible when $|x - y|$ is less than a critical value $|x - y|_c$. The observed range of miscibility, in contrast, depends on the copolymer chemical compositions x and y in addition to a dependence on $|x - y|$. The monomer sequence distribution along the copolymer chain is examined by NMR spectroscopy which shows that the copolymers used in this study are far from purely random. For norbornene contents lower than 50%

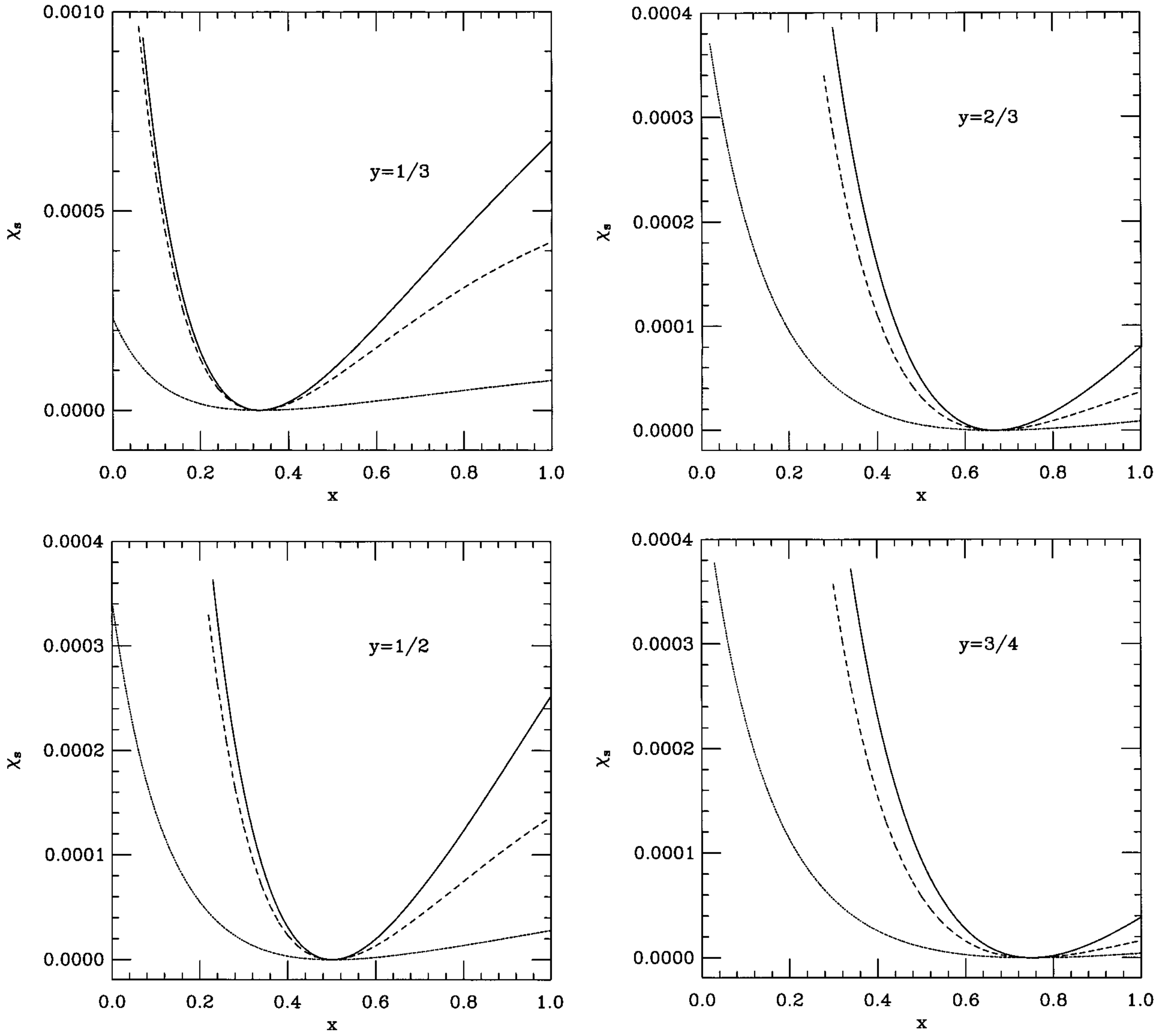


Figure 5. Computed entropic protion χ_s of the interaction parameter for N_xE_{1-x}/N_yE_{1-y} blends as a function of the composition *x* for a fixed composition *y* (as indicated in the figure.) Solid, dashed, and dotted lines refer to the LCT computations performed for models of norbornene/ethylene chains with fully flexible bonds, with stiff norbornene side groups, and with semiflexible backbone, respectively. The dimensionless exchange energy is taken as $\epsilon/kT = 0.002$ for all three models, while the dimensionless bending energy is $E_b/kT = 0.7$.

($x, y < 0.5$), the copolymer chain mostly contains isolated and alternating norbornene sequences along with norbornene dyads, while norbornene dyads and triads are the predominant sequences for higher norbornene contents.

The extension of the LCT to random copolymer systems has been applied to the N_xE_{1-x}/N_yE_{1-y} system in view of the prior successes of the theory in explaining the molecular factors governing anomalous mixing in many binary blends. The theory for random copolymers, which will be described in more detail elsewhere,[30] has been developed on a simple level that is readily usable by experimentalists. The theory is based on united atom models for individual monomers and includes an explicit computation of the entropic portion χ_s of the interaction parameter. The computations are performed for three different models to assess the relevance of stiffness in the norbornene monomer and of steric interactions between successive norbornene monomers. The theory introduces a number of approximations, such as treating the blend as incompressible, ignoring the dependence of the contact probabilities on monomer structure, using a rather simple structure for the norbornene monomer, etc. Thus, the goal of the theory is to elucidate general physical trends (rather than providing quantitative descriptions) as follows:

(a) The miscibility of the N_xE_{1-x}/N_yE_{1-y} blends is mostly determined by the entropic portion χ_s of the interaction parameter.

(b) While two of the models used are insensitive to the monomer sequence distribution, the presence of stiffness either in the norbonene side group or in the chain backbone has been found to enhance the miscibility of the ethylene/norbornene copolymers in the direction observed experimentally. The third model explicitly introduces a sequence dependence.

(c) The computed miscibility diagrams (Figures 6 and 7) compare rather well with experimental data. The two LCT models with chain stiffness both agree with the observed miscibility for all but two experimental samples. The theory, however, cannot explain the presence of the multiple miscibility windows that are observed for *x* (or *y*) = 0.361.

(d) The first two LCT models just contain a single adjustable parameter, while the third model employs

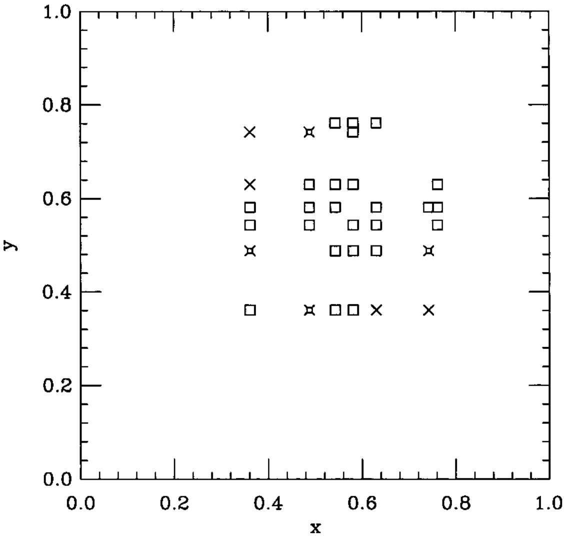


Figure 6. Comparison of experimental data with LCT calculations for equal weight fraction binary blends of N_xE_{1-x} and N_yE_{1-y} random copolymers modeled as chains with rigid norbornene side groups. Squares and crosses denote the compositions (x,y) for which the system is computed to be miscible and immiscible, respectively. The fancy squares and crosses indicate the compositions where the miscibility is predicted incorrectly. The dimensionless exchange energy is taken as $\epsilon/kT = 0.003$, and the molecular weights for all samples are summarized in Table 2.

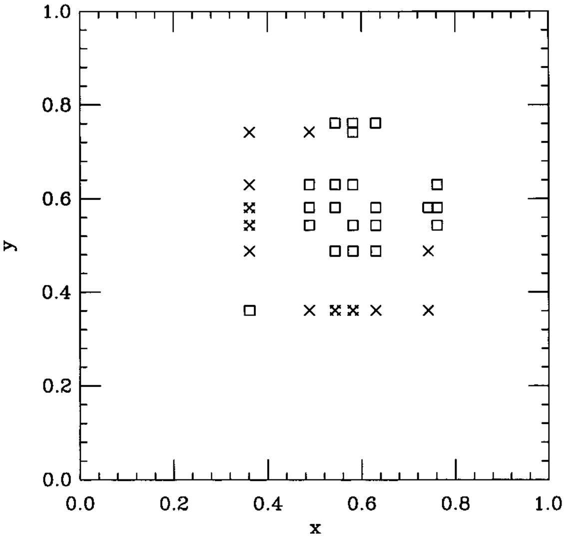


Figure 7. The same as in Figure 6 but for the model where random copolymer chains contain semiflexible backbone bonds whenever two norborene monomers are adjacent. The dimenisonless exchange energy is taken as $\epsilon/kT = 0.008$, and the dimensionless bending energy is $E_b/kT = 0.7$. The results are fairly insensitive to the value of E_b/kT over the range between 0.2 and 2.

two adjustable parameters. These models, therefore, contain fewer parameters than other theories designed to explain departures from random copolymer FH theory.

The limitations of the theory clearly arise from the multiple approximations mentioned above. Some approximations, such as blend incompressibility, are readily lifted, but other improvements, such as the dependence of the enthalpic portion χ_h on monomer structures, require complicated calculations. On the other hand, the experimental samples exhibit large polydispersity and nonrandom sequence dependence

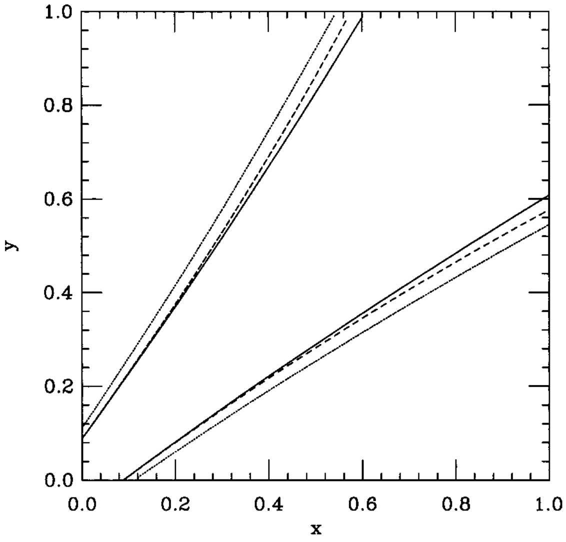


Figure 8. Phase boundaries $y = y(x)$ for the miscibility of equal volume fraction binary N_xE_{1-x}/N_yE_{1-y} blends as computed from the LCT. Solid, dashed, and dotted lines refer to the LCT calculations performed for models of norbornene/ethylene chains with fully flexible bonds, with rigid norbornene side groups, and with semiflexible backbones, respectively. The dimensionless exchange energy is taken as $\epsilon/kT = 0.003$ for all three models, while the dimensionless bending energy is chosen as $E_b/kT = 0.7$ for the third model. The polymerization indices N_1 and N_2 are assumed to be identical and equal to 10^3 for all x and y.

which may affect the miscibility behavior of some blends whose compositions lie near one of the miscibility boundaries.

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