

Molecular Interactions and Packing in Molecular Alloys between Nonisomorphous Plastic Phases

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The experimental two-component phase diagram for the plastic crystals tris(hydroxymethyl)aminomethane (TRIS) and pentaerythritol (PE) has been established from 293 K to the liquid state using thermal analysis and X-ray powder diffraction at several temperatures. The miscibility and the intermolecular interactions of the mentioned system and other related binary systems formed from compounds which present also nonisomorphous plastic phases are discussed on the basis of the steric conditions (similarity of the unit-cell dimensions and of the size and shape of the molecules) and of the other factors governing the structural arrangements such as the effects of the orientational disorder. The evolution of the packing coefficient as a function of the composition in each two-component system is analyzed to attain further understanding of the intermolecular interactions in orientationally disordered pure and mixed crystals. © 1996 Academic Press, Inc.

1. INTRODUCTION

Simple organic compounds with molecules of almost globular shape possess molecular reorientational freedom within a certain range of temperatures. The phase showing orientational disorder is called the plastic phase (1, 2) and such compounds are known as plastic crystals or orientationally disordered crystals (ODICs) (3). These crystals exhibit low values of the entropy of fusion (typically less than $2.5R$, R being the gas constant), whereas large enthalpy and volume changes are observed for the order-disorder transition between the positionally and orientationally ordered low-temperature phase and the orientationally disordered high-temperature phase.

There is growing interest in elucidating the molecular interactions in both polar and nonpolar compounds which exhibit orientationally disordered phases. In particular compounds whose molecules present some groups able to form strong interactions by means of the hydrogen bonds have been largely studied by different techniques (4–10). Some of these studies (basically NMR (4, 9) and dielectric relaxation (10) conclude that, for example, the characteris-

tic relaxation times of the overall molecular tumbling in the plastic phases are considerably high when compared to similar molecules lacking of this kind of interactions. Nevertheless, it was early thought that a packing parameter, i.e., the ratio of the volume of the molecule in a crystal unit cell to its occupied overall volume, lower than 0.63 should be a necessary condition to get the orientational freedom (overall or uniaxial rotation) of the molecules (11).

Two of the aims of the present work are to emphasize the usefulness of investigating molecular alloys in order to obtain more light on molecular interactions in plastic phases and, at the same time, to establish the compatibility between a high value of the packing parameter and the existence of molecular orientational freedom. To do so, the binary phase diagram between two compounds, both plastic crystals, will be presented in this work. The compounds, PE, pentaerythritol, and TRIS, tris(hydroxymethyl)aminomethane, are tetrahedral molecules whose low temperature solid forms are governed by strong interactions due to hydrogen bonds (12–14).

This study must be also located in a more general framework, the object of which is to evaluate the most important elements controlling the syncrystallization between two components, that is, the steric factors and the intermolecular interactions (15).

2. EXPERIMENTAL

2.1. Diffraction as a Function of Continuous Heating

Powder diffraction patterns as a function of the continuous evolution of the temperature were taken by means of a Guinier–Simon camera. The experimental conditions and the details of the procedure have been described in a previous work (16).

2.2. Diffraction at Constant Temperature

X-ray powder diffraction measurements were performed at constant temperature using a Siemens D-500 vertical

diffractometer equipped with an Anton Paar temperature camera. The details of the experimental conditions and the procedure have been carefully described elsewhere (16, 17).

Lattice parameters were obtained by a least-squares refinement method (18) after the indexing of the patterns.

2.3. Thermal Analysis

The thermal measurements were performed by means of a Perkin–Elmer DSC-7 instrument, using ca. 5 mg samples in hermetically sealed pans under a nitrogen atmosphere. The scanning rate used was 2 K min⁻¹.

2.4. Materials

Both TRIS and PE materials were purchased from Aldrich with purities of 99.9+% and 99%, respectively. Following the standard procedures (19, 20), PE was purified several times by recrystallization from its aqueous solution followed by long and careful drying.

2.5. Molecular Alloys

The samples were prepared from the melt of the two initial materials in the selected proportions by slow cooling to room temperature.

3. RESULTS

3.1. Materials

3.1.1. TRIS

The crystal structure of the low temperature solid form (phase II) was fully determined as orthorhombic [O] space group $Pn2_1a$ with $Z = 4$ [13, 21]. The refined lattice parameters at 293 K have been previously reported by us as $a = 8.853(3)$ Å, $b = 7.804(2)$ Å, and $c = 8.800(3)$ Å (22). At 406.8 ± 1.0 K TRIS transforms to the high temperature solid form or plastic phase (phase I). This phase (hereafter called C_1), stable up to melting at 442.7 ± 1.0 K, was found to be body centered cubic (space group $Im3m$ with $Z = 2$) by means of a single crystal study (13). The lattice parameter of this disordered phase was determined to be $6.888(8)$ Å at 408 K (23). The scattering of the lattice parameters found in the literature is considerably higher for phase I than for phase II due to its high symmetry and highly disordered structure. Nevertheless, the highest differences are ca. 0.5%. The enthalpy variations for phase II to I and I to liquid transitions are 34.0 ± 1.7 and $3.7 \pm .2$ kJ · mol⁻¹, respectively. Both transition temperatures and enthalpy changes are in close agreement with those found in previous works (24–26).

3.1.2. PE

At room temperature (phase II) PE is tetragonal [Q], space group $I\bar{4}$ with $Z = 2$ according to reported work

(12, 27). Our refined lattice parameters determined at 293 K are $a = 6.086(2)$ Å and $c = 8.745(3)$ Å (28). The transition from the low temperature solid form to the high temperature disordered form (phase I) takes place at 460.7 ± 1.0 K. Phase I is known to be face centered cubic ($Z = 4$) (29) with lattice parameter of $9.045(11)$ Å at 503 K (30). This plastic phase transforms to the liquid state at 539.0 ± 1.0 K. The melting temperature agrees with the previously published works where the material was submitted to a careful purification process (30, 31). The enthalpies for the II to I and I to liquid transitions are 40.0 ± 2.0 and 5.2 ± 0.3 kJ · mol⁻¹, respectively.

3.2. Molecular Alloys

3.2.1. Crystallographic Characterization

a. Diffraction as a function of continuous heating. In Fig. 1 we show the Guinier–Simon patterns corresponding to the samples with PE mole fraction (X) of 0.35, 0.40, and 0.45, in addition to those of the pure compounds TRIS ($X = 0$) and PE ($X = 1$), in order to present the phase or the coexisting phases in equilibrium at each temperature.

Both 0.35 and 0.40 mixed samples show the same basic features: (i) the existence of a two-phase domain [O + Q]; (ii) the disappearance of the reflections corresponding to the orthorhombic lattice and the appearance of reflections of the body centered cubic C_1 giving rise to a [Q + C_1] domain at a similar temperature for both samples, ca. 400 K; (iii) disappearance of the [Q] phase and appearance of the C_F phase, i.e., the two-phase domain changes to the [C_1 + C_F] at ca. 424 K. For the pattern of the sample with $X = 0.35$ the coexisting phases [C_1 + C_F] transform, upon increasing temperature, to the [C_F + L] domain and finally to the [L].

For the sample with $X = 0.40$, as distinguished from the former, the C_F + C_1] domain changes to the one-phase domain [C_F] at ca. 431 K. The beginning of melting [C_F + L] and the end of the melting process are also detected.

As a consequence of the above patterns some relevant characteristics of the binary phase diagram can be inferred. First, the changes from the [O + Q] to [C_1 + Q] and [C_1 + Q] to [C_1 + C_F] at similar temperatures (ca. 400 K and 424 K, respectively, for both samples, 0.35 and 0.40, indicate the existence of two invariants. Both of them take place at lower temperatures than the transformations [O] to [C_1] and [Q] to [C_F] corresponding to the pure compounds, indicating that both are of eutectoid type. Second, the existence of the [C_1 + C_F] two-phase domain followed upon increasing temperature by the [C_F + L] two-phase domain for sample 0.35 at a temperature higher than the melting of the TRIS component establishes doubtless the appearance of a third invariant of the peritectic type. The transformation [C_1 + C_F] to [C_F] for the sample $X = 0.40$ delimits the right point of the peritectic invariant.

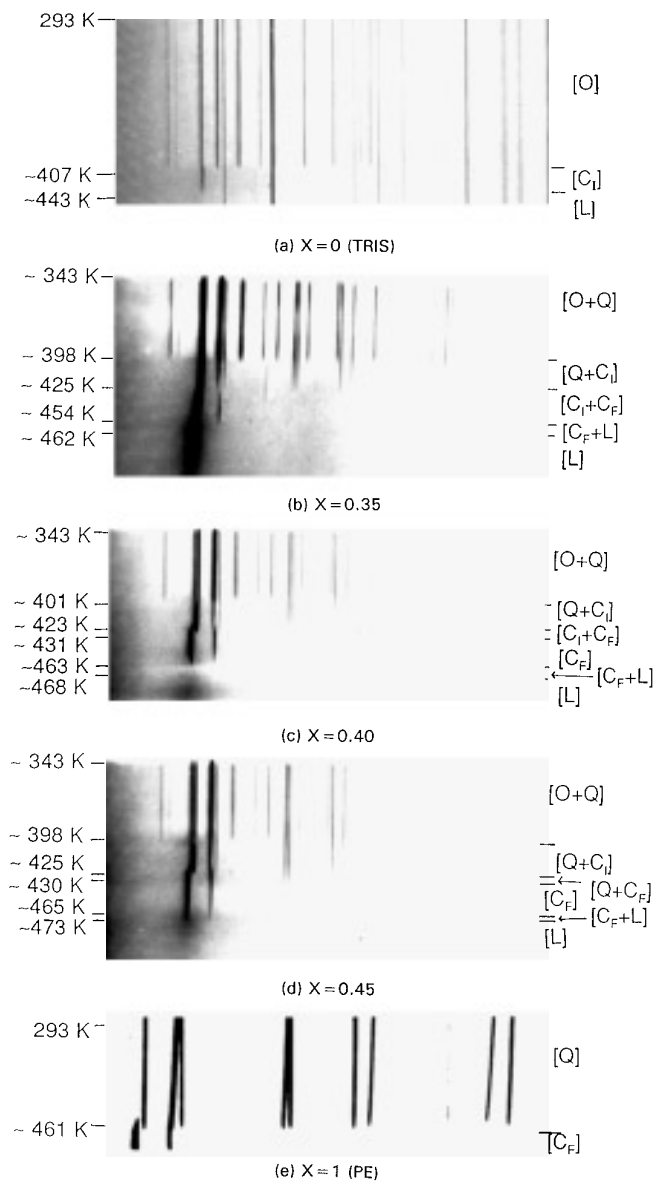


FIG. 1. Guinier-Simon patterns corresponding to the pure compound TRIS (a), the samples $X = 0.35$ (b), $X = 0.40$ (c), and $X = 0.45$ (d), and the second pure compound PE (e)

The included pattern corresponding to the sample with $X = 0.45$ reinforces the assumptions of the two eutectoid invariants and supports the former limit for the peritectic one.

In order to determine the solubility boundaries of the two-phase domains X-ray powder diffraction studies at different temperatures were undertaken.

b. Study at 293 K. As shown in the former section, below ca. 400 K a two-phase domain $[O + Q]$ exists. To determine the limits of this demixing region, we depict in Fig. 2 the evolution of the (101) and (112) reflections

corresponding to the orthorhombic [O] and tetragonal [Q] phases, respectively, vs concentration. The figure shows that, whatever the composition of the studied sample, both [O] and [Q] phases are detected, proving that the miscibility at 293 K can be assumed to be negligible.

The refined lattice parameters of the solid solutions corresponding to the solubility boundaries are very close to those of the pure compounds as a consequence of the large miscibility gap. They have been determined to be $a = 8.845(3) \text{ \AA}$, $b = 7.803(3) \text{ \AA}$, and $c = 8.807(5) \text{ \AA}$ for the orthorhombic solid solution and $a = 6.074(3) \text{ \AA}$ and $c = 8.755(4) \text{ \AA}$ for the corresponding solution at the tetragonal limit.

c. Study at 408 K. The aim of the X-ray powder diffraction measurements at 408 K is to delimit the demixing region $[Q + C_1]$ between the two eutectoid invariants.

Figure 3a depicts the evolution of the Bragg angles of the (110) reflection corresponding to the bcc lattice as a function of the mole fraction of PE. From this result the solubility boundary was determined to be 0.13 (molar fraction of PE); i.e., the limit solid solution is $\text{TRIS}_{0.87}\text{PE}_{0.13}$ ($S_A(T = 408 \text{ K}) = 0.87$).

In the same manner from the evolution of the (002) reflection of the tetragonal lattice, the solubility of TRIS in the PE has been determined (figure 3b) as the solid solution $\text{TRIS}_{0.17}\text{PE}_{0.83}$ (i.e., $S_B(T = 408 \text{ K}) = 0.83$).

Table 1 contains the cubic parameter for the molecular alloys of phase C_1 and the lattice parameters corresponding

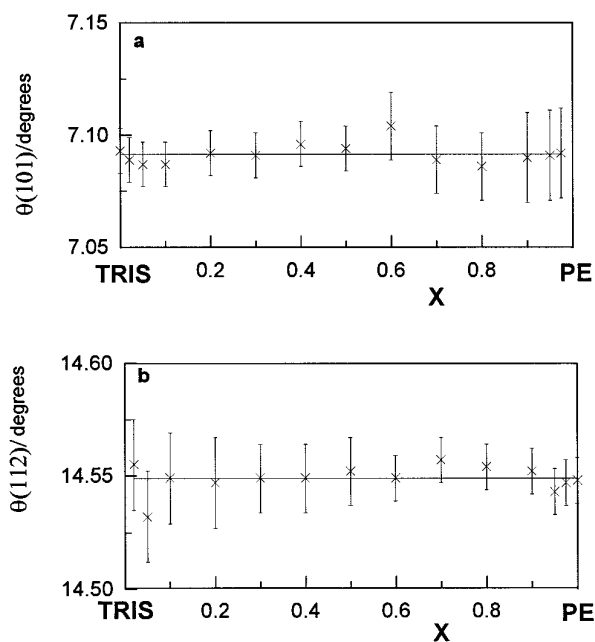


FIG. 2. Bragg's angles (θ ($^\circ$)) as a function of concentration of PE for the (101) (a) and (112) (b) reflections corresponding to the orthorhombic and tetragonal lattices respectively, at 293 K.

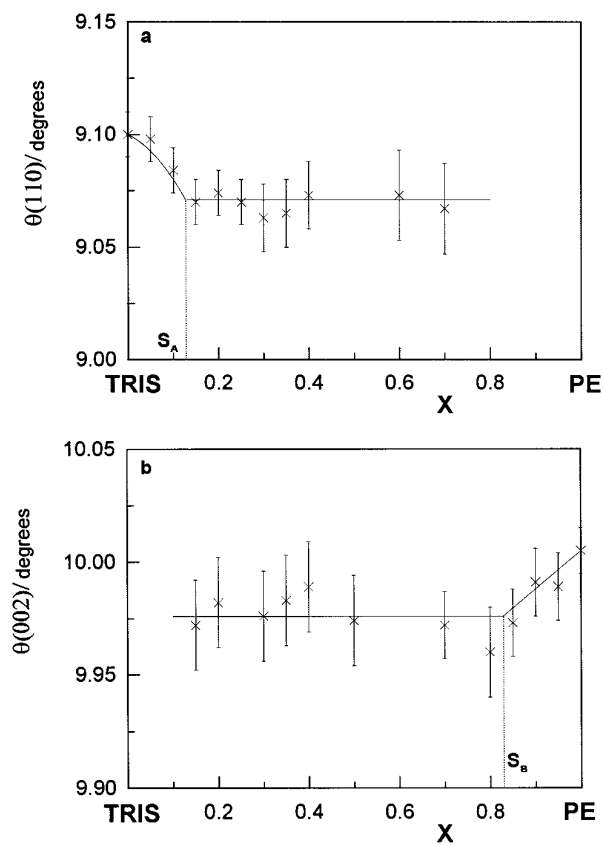


FIG. 3. Evolution of the Bragg's angle (θ ($^\circ$)) vs concentration for the (110) (a) and (002) (b) reflections corresponding to the bcc and tetragonal lattices, respectively, at 408 K.

TABLE 1
Lattice Parameters and Volume Occupied by One Molecule for the Pure Compounds, Their Alloys, and the Limiting Solid Solutions at 408 K as a Function of the Mole Fraction of PE

X	$a/\text{\AA}$	$c/\text{\AA}$	$V/Z/\text{\AA}^3$
0(TRIS)	6.888(8)		163.4(5)
0.05	6.889(8)		163.5(5)
0.10	6.900(8)		164.3(5)
$S_A = 0.13$	6.910(8)		165.0(5)
$S_B = 0.83$	6.081(3)	8.897(4)	164.5(2)
0.85	6.074(3)	8.889(5)	164.2(2)
0.90	6.081(3)	8.889(4)	164.4(2)
0.95	6.092(3)	8.875(4)	164.7(2)
1 (PE)	6.092(3)	8.869(3)	164.6(2)

to the alloys of tetragonal structure at 408 K. The volume occupied by the average molecule (V/Z) is also included for each lattice. As can be seen from these values, there is no significant change in V/Z for the alloys in the solid ordered form Q, whereas when the larger PE molecule is introduced in the host bcc lattice, a significant increase of the lattice volume is observed. This experimental result has been also found in previous work (22, 23, 32) and it seems to be a general rule: the deformation of the unit cells of the low temperature ordered solid forms is always less than the deformation of the high temperature orientationally disordered forms (i.e., plastic phases).

The next two sections are devoted to the determination of the immiscibility gap between the disordered forms and

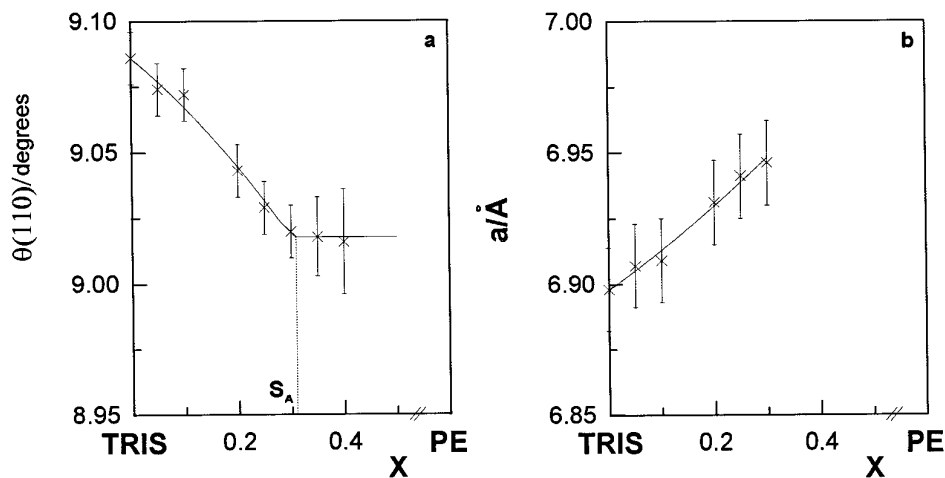


FIG. 4. Evolution of the Bragg's angle (θ ($^\circ$)) for the (110) reflection (a) and lattice parameter (a (\AA)) (b) vs concentration for the bcc phase C_1 at 428 K.

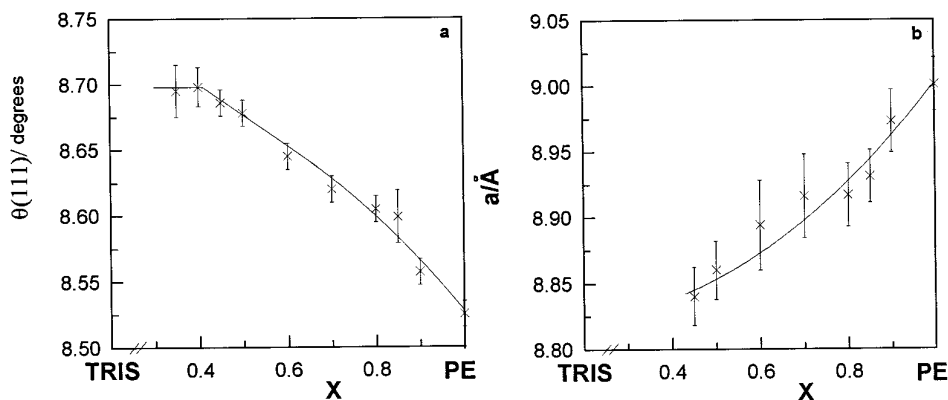


FIG. 5. Evolution of the Bragg's angle (θ ($^\circ$)) for the (111) reflection (a) and lattice parameter (a (\AA)) (b) vs concentration for the fcc phase C_F at 453 K.

to analysis of the evolution of the unit cell parameters in the molecular alloys as a function of the mole fraction. For the last determination the same temperature should be used when possible. Nevertheless, in the present case the melting temperature of TRIS (444.7 K) is lower than the transition temperature of PE (460.7 K), making infeasible the study at a given temperature for both. Thus two temperatures (as low as possible in order to diminish the error in the lattice parameter determination) had to be chosen, the first one at 428 K for the bcc alloys (just above the second eutectoid invariant) and the second at 453 K for the fcc alloys. In this last case, alloys with mole fraction

from 0.85 to 1 were undercooled to keep the fcc phase at that temperature.

d. Study at 428 K. In Fig. 4a the Bragg angles of the (110) reflection for the bcc (C_I) is given as a function of the mole fraction of PE. From it, the solubility boundary was determined to be $S_A(428 \text{ K}) = 0.31$ molar fraction of PE. Figure 4b shows the lattice parameters for the bcc alloys.

e. Study at 453 K. In Fig. 5 the Bragg angle of the (111) reflection of the fcc phase (C_F) together with the lattice parameters for these fcc alloys vs concentration are depicted. Following the same procedures as described above the solubility of TRIS in PE was determined to be $S_B(T = 453 \text{ K}) = 0.41$ (molar fraction of PE).

In Table 2 we give the lattice parameters and the volume occupied by one molecule for the initial materials and their alloys, at 428 K for the bcc and at 453 K for the fcc alloys.

TABLE 2

Lattice Parameters and Volume Occupied by One Molecule for the Pure Compounds, Their bcc and fcc Alloys, and Their Corresponding Limiting Solid Solutions at 428 K and 453 K, Respectively, as a Function of the Mole Fraction of PE

X	T/K	Phase	$a/\text{\AA}$	$V/Z/\text{\AA}^3$
0(TRIS)	428	$[C_I]$	6.898(8)	164.1(6)
0.05	428	$[C_I]$	6.907(8)	164.8(6)
0.10	428	$[C_I]$	6.909(8)	164.9(6)
0.20	428	$[C_I]$	6.931(8)	166.5(6)
0.25	428	$[C_I]$	6.941(8)	167.3(6)
0.30	428	$[C_I]$	6.946(8)	167.6(6)
$S_A = 0.31$	428	$[C_I]$	6.951(8)	167.9(6)
$S_B = 0.41$	453	$[C_F]$	8.824(10)	171.7(5)
0.45	453	$[C_F]$	8.840(11)	172.7(5)
0.50	453	$[C_F]$	8.860(17)	173.9(6)
0.60	453	$[C_F]$	8.894(17)	175.9(6)
0.70	453	$[C_F]$	8.916(16)	177.2(6)
0.80	453	$[C_F]$	8.917(12)	177.3(6)
0.85	453	$[C_F]$	8.931(10)	178.1(6)
0.90	453	$[C_F]$	8.973(12)	180.6(6)
1(PE)	453	$[C_F]$	9.001(10)	182.3(6)

3.2.2. Thermal Analysis

The characteristic temperatures of the transitions measured using the DSC were determined, from the original thermograms, using the shape factor method (33, 34).

The temperatures of the solid–solid transitions together with the melting transitions are shown in Table 3.

3.2.3. Phase Diagram

By synthesizing the information obtained from thermal analysis and x-ray diffraction patterns as a function of continuous heating, together with the solubility limits determined by x-ray diffraction at different temperatures, the experimental phase diagram shown in Fig. 6 is obtained.

The main characteristics of the PE/TRIS two-component system are the existence of two eutectoid and one peritectic invariants, the parameters of which are summarized in Table 4.

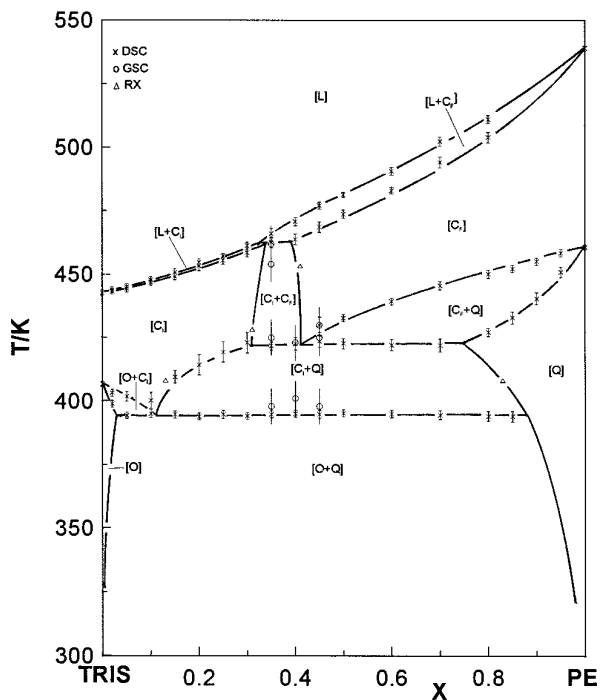


FIG. 6. Phase diagram of the binary system PE/TRIS: (x) DSC, (o) Guinier-Simon technique, (Δ) solubility boundaries determined by X-ray powder diffraction at constant temperature.

4. DISCUSSIONS AND CONCLUSIONS

The ordered form of PE has been considered as a model compound for the other members of the series of poly(hydroxymethyl) compounds and, as such, it has been studied by several techniques (12, 27, 35, 36). Also, TRIS has been the subject of many studies (13, 21–26, 37–39), particularly with vibrational techniques (14, 39) in order to account for the differences between CH_2OH and NH_2 interactions. Some NMR studies and, more recently, infrared and Raman spectra (37, 14) suggest that the hydrogen bonding scheme present in the ordered low temperature phase plays an important role in the plastic phase. To throw light on the influence of the hydrogen bonds in plastic phases, the modification of the molecular surroundings can be achieved by progressive substitution of the neighbor molecules on the same lattice, i.e., the formation of molecular alloys. In this context the investigation of the two-component mixed crystals TRIS/PE is particularly interesting and, as shown in the previous part of this work, the existence of relatively large domains of miscibility makes it possible to analyze the influence of the molecular interactions and, at the same time, to study the geometric factors ruling the miscibility. To do so, the binary systems previously studied by us between related poly(hydroxymethyl) compounds such as NPG/AMP (32), PG/TRIS (23) and

NPG/TRIS (22)¹ can be used to reinforce some conclusions for the system described in this work and to obtain some common behavior. For all the systems mentioned the plastic phases of the components belong to the fcc (NPG and PG) or to the bcc (AMP and TRIS) lattice symmetry.

To account for the miscibility between two compounds, that is to say, to analyze the conditions ruling the syncrystallization, it has previously been shown (22, 40) that two essential factors must be born in mind. In order to sketch them (a more detailed discussion can be found in Ref. (22)) they can be presented as: (i) the steric factors, i.e., the shape and size of molecules and unit cell dimensions, and (ii) the molecular interactions in the pure compounds and their mixed-crystal structures.

Relating to the shape and size of the molecules considered in the formation of a molecular alloy, a coefficient of geometric similarity ϵ_K (degree of molecular homeomorphism) was earlier introduced by Kitaigorodsky (40). This parameter, calculated as $\epsilon_K = 1 - \Gamma/\Delta$, where Γ are the nonoverlapping parts and Δ the overlapping parts when the molecules are superimposed, was marked out to be above 0.85 to achieve complete miscibility in systems where isomorphism is supposed to exist between the components. In the present case (PE/TRIS) polymorphism exists in both compounds, but the low temperature solid forms, as well as the high temperature plastic phases, are nonisomorphous due to the different symmetry of the cells. In spite of this fact, although ϵ_K cannot be used for the prediction of the formation of molecular alloys whatever the analyzed phase, it can be used as a rough parameter to account for the molecular shape and size differences. To evaluate ϵ_K the interatomic distances and van de Waals atomic radii were extracted from Refs. (41–43). The values used are presented in Table 5. The two-component systems related in this work are depicted in Fig. 7. Table 6 reports the molecular volumes and ϵ_K values for the analyzed and some related systems. In spite of the low ϵ_K values for the PE/TRIS (0.89) and NPG/TRIS (0.88) systems, no substantial differences are found for the miscibility gaps when the four systems are compared in the orientational disordered phases. Two faults are known to be present in the ϵ_K coefficient. First, it is a temperature-independent and phase-independent coefficient; i.e., intermolecular interactions are not considered in its definition. Moreover, it is quite clear that in plastic phases the shape of the molecule is “missing” and, in fact only the size of the molecular envelope should be a consistent parameter to account for the geometric factor in the syncrystallization problem.

To include the whole set of factors that govern the structural arrangements (steric factors, intermolecular interac-

¹ NPG, $(\text{CH}_3)_2\text{C}(\text{CH}_2\text{OH})_2$; PG, $(\text{CH}_3)\text{C}(\text{CH}_2\text{OH})_3$; AMP, $(\text{CH}_3)\text{C}(\text{NH}_2)(\text{CH}_2\text{OH})_2$.

TABLE 3
Characteristic Temperatures for the Different Phase Transitions in the PE/TRIS Samples

X	T_{e1}/K^a	T_{sv1}/K^b	T_{e2}/K^c	T_{sv2}/K^d	$T_{solidus}/K^e$	T_{e3}/K^f	$T_{liquidus}/K^g$
0(TRIS)	(406.8 ± 1.0)				442.7 ± 1.0		
0.02	(398.9 ± 1.3)	403.3 ± 1.4			443.2 ± 1.1		443.9 ± 1.1
0.05	394.4 ± 1.2	401.9 ± 2.0			444.3 ± 1.3		445.1 ± 1.2
0.10	395.1 ± 1.6	400.3 ± 3.2			446.8 ± 1.1		447.8 ± 1.3
0.15	394.8 ± 1.4	409.6 ± 2.5			449.2 ± 1.4		450.7 ± 1.5
0.20	393.9 ± 1.4	414.3 ± 4.0			453.3 ± 1.8		454.7 ± 1.4
0.25	394.8 ± 1.6	419.4 ± 4.0			455.5 ± 1.5		457.7 ± 1.1
0.30	394.2 ± 1.3	423.0 ± 4.0			458.6 ± 1.8		461.3 ± 1.4
0.35	394.8 ± 1.3		421.7 ± 1.6			462.6 ± 2.0	466.0 ± 1.0
0.40	395.1 ± 1.4		422.6 ± 2.4		463.8 ± 2.1		470.8 ± 1.6
0.45	394.9 ± 1.5		423.5 ± 2.2	430.0 ± 3.0	468.6 ± 2.0		477.1 ± 1.4
0.50	395.3 ± 1.4		422.7 ± 2.0	432.7 ± 1.5	473.7 ± 1.6		481.4 ± 1.0
0.60	395.0 ± 1.5		422.1 ± 2.3	439.3 ± 1.4	483.1 ± 1.4		490.8 ± 1.5
0.70	394.6 ± 1.7		422.0 ± 2.5	444.5 ± 1.6	494.3 ± 2.1		502.4 ± 1.8
0.80	394.1 ± 1.9		(427.1 ± 1.6)	450.1 ± 1.6	504.0 ± 2.0		511.0 ± 1.6
0.85	394.0 ± 2.0		(432.8 ± 2.4)	452.2 ± 1.5			
0.90			(440.4 ± 2.4)	455.1 ± 1.4			
0.95			(450.9 ± 2.0)	458.4 ± 1.5			
1(PE)			(460.7 ± 1.0)		539.0 ± 1.0		

^a T_{e1} : Eutectoid invariant [O + O + C₁]. The values in parantheses are out of the invariant.

^b T_{sv1} : Temperature corresponding to the first superior solvus: Change from [O + C₁] to [C₁] for $X \leq 0.10$ and from [Q + C₁] for $X > 0.10$.

^c T_{e2} : Eutectoid invariant [Q + C₁ + C_F]. The values in parantheses are out of the invariant and correspond to the change [Q] to [Q + C_F].

^d T_{sv2} : Temperature corresponding to the second superior solvus: Change from [Q + C_F] to [C_F].

^e $T_{solidus}$: Beginning of the melting process.

^f T_{e3} : Peritectic invariant [C_F + C₁ + L].

^g $T_{liquidus}$: End of the melting process.

tions and the effects of orientational and positional disorder) the concept of degree of isomorphism, ε_m^i , has been recently defined (44). This parameter is defined in a similar way to ε_K , but superimposing the unit cells when isomorphism between the considered phases has been proved (15). The ε_m^i coefficient has been successfully used in two-component systems displaying plastic phases; in all the cases analyzed a high degree of isomorphism appears in the regions where complete miscibility was found (45). Nevertheless, the first condition for the establishment of isomorphism is the existence of the same space group for

both phases of the pure components, and in the systems analyzed in this work this requirement is not met.

As a whole, steric factors and molecular interactions can be accounted by the calculation of the packing parameter, i.e., the ratio of the volume of the molecules in the crystal unit cell to its overall volume. The volume of the molecules of the initial materials previously obtained for the determination of ε_K has been used (see Table 6). To calculate the

TABLE 5
Values of the van der Waals Atomic Radii (R), Interatomic Chemical Bond Lengths (d), and Bond Angles (β)

	H	C	N	O		
$R(\text{\AA})$	1.17	1.80	1.57	1.36		
	C-C	C-H	C-N	C-O	O-H	N-H
$d(\text{\AA})$	1.54	1.08	1.47	1.43	0.97	1.02
	C-C-H	C-C-O	C-N-H	H-N-H	C-O-H	
$\beta(^{\circ})$	110.0	107.4	109.5	104.5	106.1	

TABLE 4
Characteristic Temperatures and Concentration Values Corresponding to the Invariants of the PE/TRIS System

Invariant	X (mole fraction of PE)			T/K
	M	E	N	
Eutectoid e_1	0.03	0.11	0.88	394.6 ± 1.0
Eutectoid e_2	0.31	0.41	0.75	422.4 ± 1.0
Peritectic e_3	0.325	0.34	0.39	462.6 ± 1.0

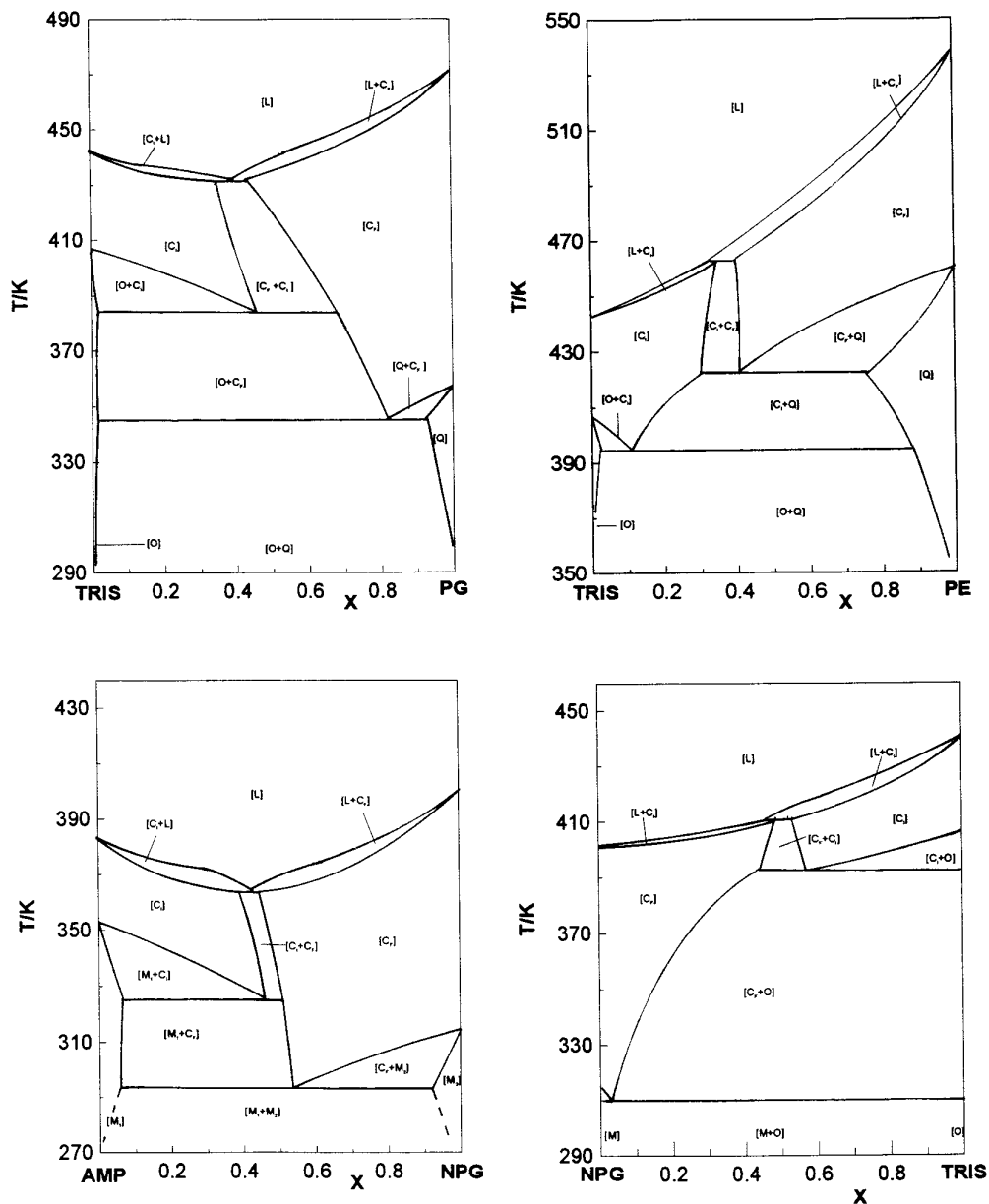


FIG. 7. Phase diagrams showing partial miscibility in plastic phase.

TABLE 6
Molecular Volumes and ϵ_K Values for the
Systems Compared

System A/B	$V_{mA}(\text{\AA}^3)$	$V_{mB}(\text{\AA}^3)$	ϵ_K
NPG/AMP	108.9	103.6	0.94 ₂
PG/TRIS	115.2	109.9	0.94 ₆
NPG/TRIS	108.9	109.9	0.88 ₁
PE/TRIS	121.4	109.9	0.89 ₀

volume of the average molecule for a given molar fraction X we can reasonably assume it to be $(1 - X)V_{m1} + XV_{m2}$, i.e., the average of the volumes of the present molecules in the alloy. Thus, the packing coefficient $\xi(X, T)$ for a molecular alloy of a molar fraction X and at a given temperature T is calculated using the expression

$$\begin{aligned} \xi(X, T) &= \frac{(1 - X)V_{m1} + XV_{m2}}{V(X, T)/Z} \\ &= \frac{1}{V(X, T)/Z} \left[(1 - X)\xi_1(T) \frac{V_1}{Z_1} + X\xi_2(T) \frac{V_2}{Z_2} \right], \end{aligned}$$

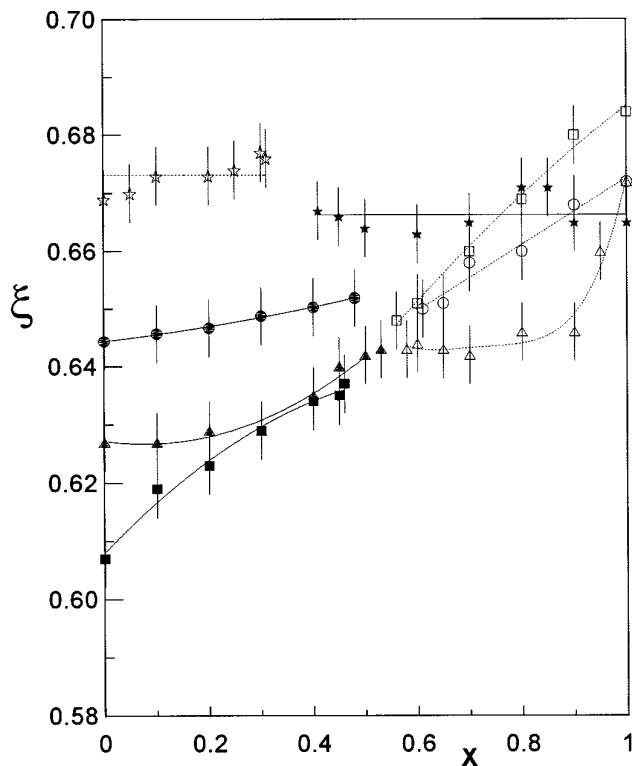


FIG. 8. Packing coefficient ξ for the bcc (empty symbols) and fcc (full symbols) molecular alloys corresponding to the systems: (■) $\text{NPG}_{1-x}\text{TRIS}_x$ (at 398 K); (▲) $\text{NPG}_{1-x}\text{AMP}_x$ (at 353 K); (●) $\text{PG}_{1-x}\text{TRIS}_x$ (at 408 K) and (★) $\text{TRIS}_{1-x}\text{PE}_x$ (at 428 and 453 K for the bcc and fcc respectively).

where V_{mi} stands for the molecular volumes of the pure components, $\xi_i(T)$ for the packing coefficients of the pure components, $V(X, T)/Z$ for the volume of the unit cell per molecule of the molecular alloy, and V_i/Z_i for the volume of the unit cell per molecule of the pure components.

Figure 8 depicts the evolution of the packing coefficient for the bcc and fcc alloys corresponding to the system PE/TRIS and the related systems. For each $A_{1-x}B_x$ system of the above figure the B component has been chosen as the molecule with a large number of CH_2OH groups. When the number of CH_2OH groups is equal for both components (NPG/AMP and PG/TRIS cases) B has been picked out as the molecule having the NH_2 group. From this figure some conclusions can be directly achieved. First, it is quite obvious that, except for the PE/TRIS system, the packing coefficient of the molecular alloys increases with increasing molar fraction. That means, owing to the previous choice of the B component that the packing in the mixed crystal structures increases when the number of CH_2OH groups in the average molecule is increased, i.e., when an enlargement of the hydrogen-bonded intermolecular interactions has been produced. In the case of the NPG/AMP and

PG/TRIS systems both A and B molecules have the same number of CH_2OH groups, the difference being the replacement of a methyl group by an amine group. As can be followed from Fig. 8, the packing coefficients in both systems are continuous increasing functions of composition in each solid solution region (fcc or bcc), proving that the NH_2 group must participate in the hydrogen bonding scheme. Moreover, in the PE/TRIS system the replacement of the host molecules (TRIS or PE) in the host structure (bcc or fcc) by the guest molecule (PE or TRIS) does not modify the packing. This implies that the intermolecular interactions in relation to the available volume lattice are identical in TRIS and PE and their molecular alloys, so that the strengths of the hydrogen bonds produced by the NH_2 group and those produced by the CH_2OH group become more or less equal in the disordered phases. The same idea was proposed in order to explain the infrared spectrum corresponding to the plastic phase of TRIS (where only one broad absorption associated to the CH_2OH and NH_2 hydrogen bonds was detected (14)). Our work reinforces this conclusion, making it evident that the replacement of a molecule of TRIS by a molecule of PE (with four $-\text{OH}$ groups) does not affect the molecular packing.

On the other hand, the values plotted in Fig. 8 shown that the existence of molecular orientational freedom is perfectly compatible with a relatively high packing (in particular higher than 0.63, as was previously established in Ref. (11), this conclusion being valid for pure compounds as well as for their mixed crystal structures.

Finally, we want to emphasize that although orientational disorder and dynamics in one-component organic crystals have been extensively studied using various experimental techniques as well as by computer simulation, only a very few investigations in binary systems have been performed to date (9, 22, 23, 32, 46, 47). More light on the two types of motional processes found in the disordered phases (overall tumbling and translational diffusion) in two-component systems would be of great interest in investigating the dynamics of the molecular alloys. In particular, the knowledge of the evolution of the orientational ordering in a two-component system forming plastic crystals would be eminent. Unfortunately only one work analyzing this orientational order in the $(\text{CH}_3)_2\text{CCl}_2\text{-Cl}_4\text{C}$ system is known to us (47).

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