

# Poly(ethylene oxide)–poly(methyl methacrylate) interactions in polymer blends: an infra-red study\*

J. I. Marcos†, E. Orlandi and G. Zerbi‡

Dipartimento di Chimica Industriale, Politecnico, L. da Vinci 32, Milano, Italy

(Received 21 November 1988; revised 18 October 1989; accepted 21 November 1989)

Following our previous work in this field it is shown that the vibrational infra-red spectrum indicates that polyoxyethylene, usually in the most stable helical structure (H), transforms into a *trans* planar structure (T) when in contact with syndiotactic poly(methyl methacrylate) (PMMA). The conversion of solid H to solid T decreases gradually from syndiotactic PMMA to atactic PMMA to isotactic PMMA. A comprehensive interpretation is proposed in order to reconcile the detailed spectroscopic data reported here and the overall morphological descriptions reported by other authors.

(Keywords: blends; infra-red spectroscopy; morphology)

## INTRODUCTION

In this paper we reconsider the data from vibrational spectroscopy on mixtures of poly(methyl methacrylate) (PMMA) and poly(ethylene oxide) (PEO). The nature of the intermolecular interactions between these two systems is still an unresolved problem.

It was previously reported that solidification from the melt of a mixture of atactic PMMA and PEO yields a material with infra-red optical properties different from those of the starting materials<sup>1</sup>. Several authors have also reported that other physical properties of the mixture are different from those of the parent materials, thus indicating that some type of interaction takes place<sup>2,3</sup>.

The information on a molecular level reported in ref. 1 was that, when the two polymers are mixed in solution and deposited on a surface of KBr, the molecular structure of PEO, originally helical, transforms into a *trans* planar conformation. Thus it was thought that specific intermolecular interactions should occur to force the molecule to flatten into a planar structure.

In an attempt to identify these forces, the model of intermolecular electrostatic interactions (which is applicable to many simpler systems) was used<sup>4</sup>. The existence of a weak specific force between the positive charge on the C atom of the ester group and the negative charge on the oxygen atom of PEO has been postulated<sup>1</sup>. This concept implies the onset of some sort of preferential spatial pairing of the two molecules, thus requiring the consideration of a one-dimensional commensurability between the two one-dimensional polymer chains which determines the number of possible contacts.

If such a specific pairing between molecular sites takes place, blending could be influenced by the stereospecificity and chain conformational regularity of the

polymer chain<sup>1</sup>. The fact that PEO can take up a zig-zag structure in some chemical circumstances has been pointed out by other authors<sup>5</sup>. The fact that the planar structure is obtained also when PEO is in contact with PMMA is puzzling. However, it is generally accepted and it has been recently strongly stressed<sup>3</sup> that PEO easily crystallizes as crystalline lamellae of PEO variously embedded into an amorphous matrix of PMMA.

In this work we report the experimental results obtained upon blending PEO with isotactic, syndiotactic and atactic PMMA (i-PMMA, s-PMMA and a-PMMA). Further results on poly(vinyl acetate) (PVAc) will be reported elsewhere.

## EXPERIMENTAL

The origin and main physical properties of the compounds studied are the following:

(i) PEO (from Fluka);  $M_w = 20\,000$ ;  $T_m = 65^\circ\text{C}$ ;  $T_g = 42^\circ\text{C}$ .

(ii) a-PMMA (from BDH);  $M_w = 116\,000$ ;  $T_g = 100\text{--}110^\circ\text{C}$ .

(iii) i-PMMA (from Polymer Laboratories);  $M_w = 178\,372$ ;  $T_g = 45^\circ\text{C}$ ; steric composition from n.m.r., 90% isotactic, 6% heterotactic and 4% syndiotactic.

(iv) s-PMMA (from Polymer Laboratories);  $M_w = 262\,300$ ;  $T_g = 118^\circ\text{C}$ ; 6% isotactic, 18% heterotactic and 78% syndiotactic.

The infra-red spectra were recorded with a Nicolet 7199 interferometer at  $1\text{ cm}^{-1}$  resolution. Each spectrum reported is the result of the co-addition of 256 scans. Data manipulations were carried out with standard programs. The main attention in this work was paid to accurate spectral subtractions.

The binary mixtures of 3:1 PEO/PMMA were prepared as cast films from solution of  $\text{CHCl}_3$  on a KBr disc in the following conditions:

(a) at room temperature;

(b) evaporation at room temperature and annealing at  $50^\circ\text{C}$  for 6 and 48 h;

\* Work presented at the meeting of the American Physical Society, Baltimore, 1985

† Permanent address: Departamento de Química Física, Universidad de Málaga, 29071-Málaga, Spain

‡ To whom correspondence should be addressed

(c) evaporation at room temperature followed by heating under vacuum at 70°C for 24 h, reheating at 80°C for 15 min and annealing at 50°C for 6 and 48 h.

The method of preparation is the same as that of ref. 2 and is very similar to that of ref. 3.

The same experiments were also done with only pure PEO. In order to obtain the spectrum of the fully amorphous material, the spectrum of PEO melt was recorded with a cell heated at ~70°C.

We did not carry out any measurement of crystallinity in our samples. The data reported in refs. 2 and 3 for samples prepared in a way similar to ours indicate that, while the mixtures PEO/a-PMMA and PEO/s-PMMA form and remain miscible blends in the composition ratio used in this work, PEO/i-PMMA shows some anomalies. Moreover, in ref. 3 from d.s.c. measurements an index of crystallinity is given as  $X_c = 90, 60, 64$  and  $54$  for pure PEO, PEO/a-PMMA, PEO/i-PMMA and PEO/s-PMMA respectively.

### STRUCTURAL PROPERTIES OF PEO AND PMMA

For a better understanding of the discussion that follows we recall here the structural properties of the materials as derived from diffraction studies and from energy minimization calculations.

The thermodynamically more stable structure of PEO is a 7/2 helix with an identity period of 19.8 Å. The rotational angles of the OCCO and CCOC units are 64°58' and 188°15' respectively. Practically the conformational sequence is of the type  $TTG^{5-7}$ . It has been found, however, that the PEO molecule is very flexible, as shown when PEO makes complexes with urea, thiourea and HgCl<sub>2</sub>. In particular a planar zig-zag structure has been observed in samples under tension or when water is added<sup>8</sup>. The repeat distance of *trans* planar PEO is 7.12 Å, with triclinic unit cell<sup>8</sup>.

For simplicity the helical and *trans* planar structures will be indicated with H and T respectively. The energy difference between H and T structures is calculated to be only ~0.1 kcal mol<sup>-1</sup>, thus indicating the high molecular flexibility of PEO<sup>9</sup>.

We next consider the molecular structures of i-PMMA and s-PMMA. The structures of i-PMMA and s-PMMA have been much studied and may still be a matter of further studies because the position in space of the ester groups does strongly affect the conformation of the backbone. Furthermore since the C=O group of the ester group possesses a large dipole moment, it may easily interact with the environment through dipole-dipole coupling, thus establishing preferential interactions, which force the backbone to take up different conformations. The calculations performed on the molecule *in vacuo* (i.e. considering only intramolecular forces) must be taken only as indications of likely structures, which may change drastically when the molecule is embedded in a bulk material. An example is the 'curved' structure proposed by Vacatello and Flory<sup>10</sup>, mentioned also in ref. 3 for s-PMMA, and the *trans* planar structure observed by Dybal *et al.* when s-PMMA self-associates with itself<sup>11</sup>.

We consider the structure of s-PMMA in the solid as still an unsettled problem. We think, however, that the 'curved' structure proposed by Vacatello and Flory may eventually exist in solution or in the melt, but it must

take up another conformation in the bulk. The *trans* planar structure seems to be a likely candidate for the structure of crystalline s-PMMA.

The structure of i-PMMA has been shown to consist of a double-stranded helix in which each chain has 10 chemical units in one turn in the period of 20.8 Å. Of more interest for us is the sequence of torsional angles in the backbone, being -179° and -148°<sup>12</sup>.

### EXPERIMENTAL RESULTS AND DISCUSSION

#### Pure PEO

The unquestionable experimental fact is that by casting a film of PEO from solution of CHCl<sub>3</sub> at room temperature the infra-red spectrum shows a multiplicity of lines which resolves into a simpler spectrum upon annealing. This is an experimental proof that the as-cast film contains at least two kinds of PEO with different molecular conformations. By difference spectroscopy we have isolated the two forms, as clearly shown in Figure 1. The group-theory approach discussed in ref. 1 shows that the spectrum in Figure 1A is that of a helical structure while that in Figure 1B corresponds to a *trans* planar conformation which contains a centre of symmetry. The spectrum of a conformationally irregular PEO chain ('amorphous') is shown in Figure 1C.

The most characteristic bands of the T structure are located at 1341 (CH<sub>2</sub> wagging), 1241 (CH<sub>2</sub> twisting) and 962 cm<sup>-1</sup> (CH<sub>2</sub> rocking) and those of the H structure at 1358 (CH<sub>2</sub> wagging), 1280 and 1235 (CH<sub>2</sub> twisting), 950 and 844 (CH<sub>2</sub> rocking) and 1060 cm<sup>-1</sup> (coupled C-O

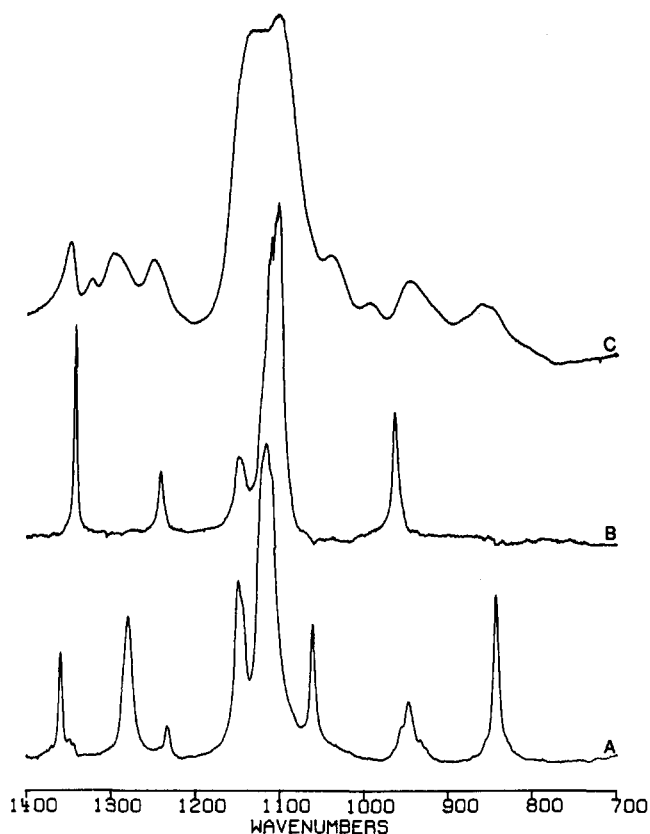


Figure 1 Infra-red spectra in absorbance scale of poly(oxyethylene): (a) in the helical (H) structure, (b) in the *trans* (T) structure and (c) in the melt state. Spectra in (a) and (b) are obtained from the mixture of the two modifications by optical subtraction

stretching and C-C stretching). Other strong lines are more or less in common with the two conformational modifications and are not taken as characteristic.

#### Spectra of the binary mixtures

The first immediate observation in the spectra of all the binary mixtures is that one finds the existence of both T and H structures with varying concentrations.

We have studied in detail the spectra of the binary mixtures PEO/i-PMMA, PEO/s-PMMA and PEO/a-PMMA in the ratio 3:1 PEO/PMMA. Since we wish to be more quantitative we measured the peak intensity  $I_{\max}$  with respect to a suitably chosen baseline of the bands at  $1341$  and  $844\text{ cm}^{-1}$  as characteristic of T and H structures, respectively. The values of the measured ratios for the samples studied in various conditions are given in Table 1. Table 1 can be read either along each row or down each column. The absorption coefficients for T and H are assumed to be equal in pure PEO and in its blends in arriving at the figures in Table 1.

We discuss first the data of the first column related to the experiments carried out at room temperature on the as-cast films with no annealing. The spectra are shown in Figure 2. This series of results suggests immediately that s-PMMA and a-PMMA favour the formation of the T structure while i-PMMA plays a minor role. These data alone do not give conclusive evidence that s-PMMA and a-PMMA stabilize the conformation of PEO because Figure 1 shows that even pure PEO cast from  $\text{CHCl}_3$  forms T and H PEO together.

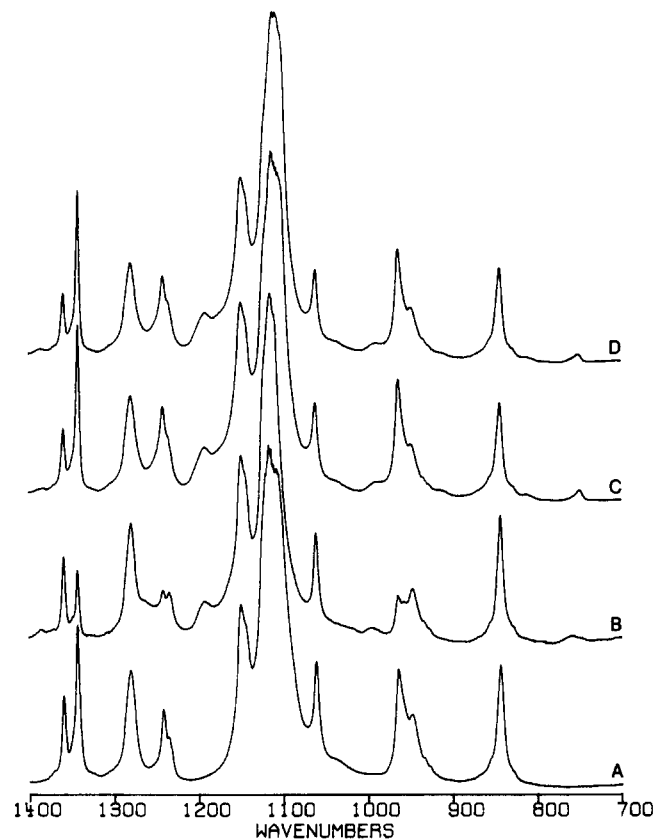
The most important information comes when the rows of Table 1 are examined. It soon becomes clear that by annealing pure T PEO quickly disappears in favour of the thermodynamically more stable H structure. On the contrary the binary mixtures show different evolution of the relative T/H content with annealing time, temperature and starting conditions of preparation. Figures 3 and 4 show that in the PEO/i-PMMA sample most PEO is in the H form but a small amount of T form is still present; s-PMMA still favours the formation of the T structure as does a-PMMA but to a smaller extent.

#### DISCUSSION

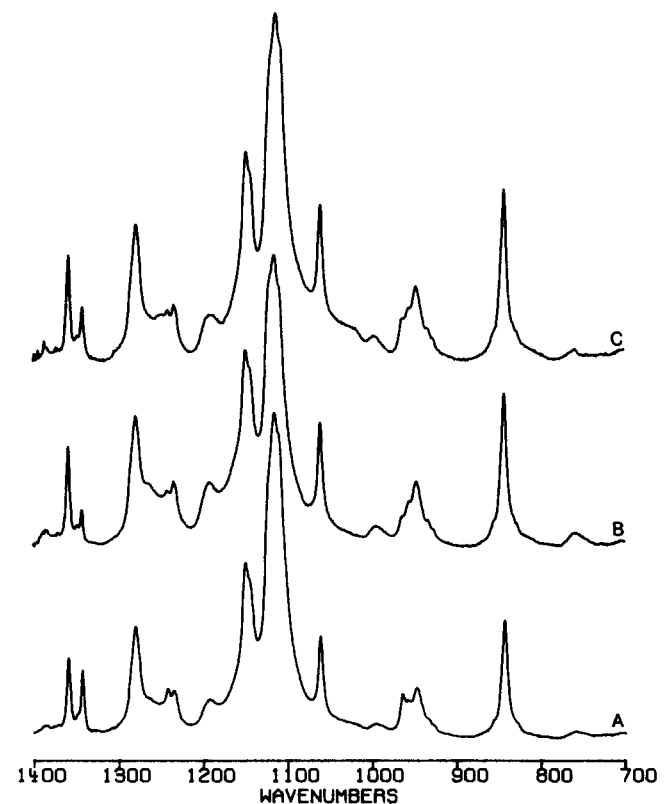
The first fact to be accounted for is that PEO alone when cast from  $\text{CHCl}_3$  shows the existence of the two conformations. Two possible situations can be envisaged. First, the cast film consists of a mechanical mixture of crystalline T and H phases; the T phase transforms into H by heating. The second possibility is that within one chain segments may take up the H or T conformation. If this were true one could be tempted to think that PEO crystallizes normally in the H form and that the T

**Table 1** Peak intensity ratios  $I(\text{trans})/I(\text{helical})$  for pure PEO and for binary mixtures of PEO and PMMA at different annealing times and temperatures (see text). (a) No annealing. (b) Annealing at  $50^\circ\text{C}$  for 6 h. (Values in parentheses refer to 48 h annealing time.) (c) Annealing at  $50^\circ\text{C}$  for 6 h after a first fast overheating as described in the text

	(a)	(b)	(c)
PEO	1.15	0.37 (0)	0
PEO/i-PMMA	0.45	0.14 (0.23)	0.14 (0.14)
PEO/s-PMMA	1.93	0.83 (0.72)	0.43 (0.90)
PEO/a-PMMA	1.76	0.46 (0.40)	0.43 (0.14)



**Figure 2** Infra-red spectra in absorbance scale of the samples as prepared whose T/H ratios are reported in the first column of Table 1: (a) pure PEO, (b) PEO/i-PMMA, (c) PEO/s-PMMA and (d) PEO/a-PMMA. The spectrum of PMMA has been subtracted



**Figure 3** Infra-red spectra in absorbance scale of PEO/i-PMMA during annealing; spectra correspond to the cases listed in the second row of Table 1. The spectrum of PMMA has been subtracted

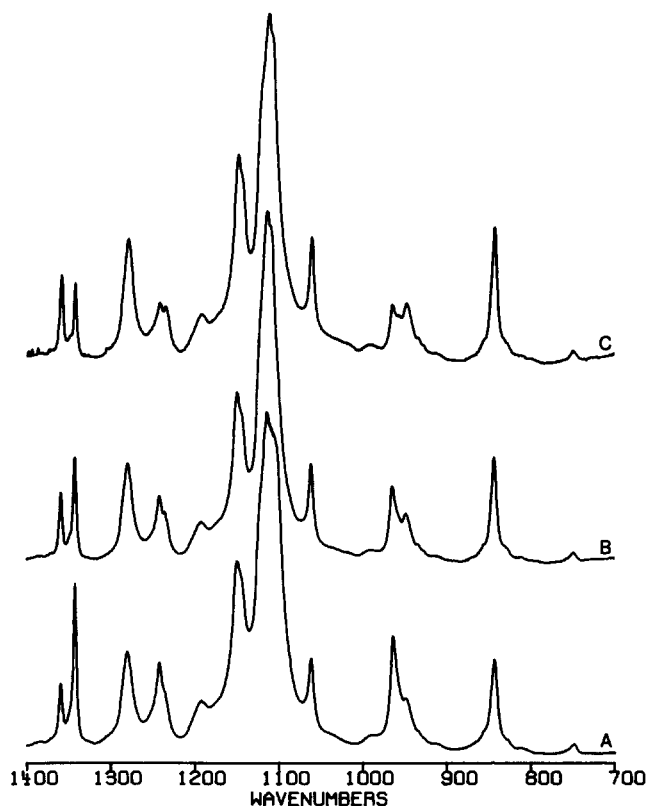


Figure 4 Infra-red spectra in absorbance scale of PEO/s-PMMA during annealing; spectra correspond to the cases listed in the third row of Table 1. The spectrum of PMMA has been subtracted

segments could be found in the 'irregular' or 'amorphous' domains of the material. This would simply mean that when the PEO chain is embedded into an irregular and/or disordered environment it likes to take the T structure. For this reason we have studied the spectrum of amorphous PEO (Figure 1C) but do not find any indication of the spectra of either H or T forms.

We have to examine in greater detail the situation of the binary mixtures of PEO and PMMA. Silvestre *et al.*<sup>3</sup> have presented a set of very interesting measurements of small-angle X-ray scattering and differential scanning calorimetry and they reach the conclusion, in agreement with ref. 1, that the tacticity of PMMA does have an influence on the structure of the blend and on the miscibility of the two polymers. They propose that in the case of PEO/a-PMMA and PEO/s-PMMA the structure consists of PEO crystalline lamellae separated by amorphous and transition regions containing PEO and PMMA, whereas the PEO/i-PMMA system consists of alternate crystalline and amorphous lamellae of PEO with i-PMMA segregated in the interfibrillar regions.

The scenario presented by Silvestre *et al.* has to be reconciled with the spectroscopic results presented in this work. The vibrational spectrum gives detailed structural information at the molecular level while it is incapable of describing what happens on the larger morphological level. At the molecular level the fact is that s-PMMA (and, to a lesser extent, a-PMMA) favours the formation of T PEO. If one accepts the fact that H PEO forms crystalline lamellae and that PMMA and PEO are confined in the interlamellar material, one should conclude that T PEO is formed for some reason when in contact with conformationally irregular PMMA. This view is, so

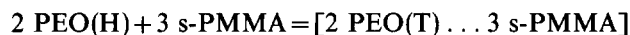
far, difficult to accept on the basis of what is presently known in the field of intermolecular interactions.

While in ref. 1 a 3/1 helix was erroneously assumed for i-PMMA, the concept of preferential pairwise electrostatic interactions between positive and negative sites of PMMA and PEO used in ref. 1 may still be valid in this case. Indeed it is hard to accept the existence of a 'curved' structure of s-PMMA in the solid<sup>3</sup>, but we wish to think of a planar zig-zag structure with an approximate repeat distance of 4.8 Å.

The possible *trans* planar structure of s-PMMA in the bulk is envisaged independently from the existence of interacting PEO molecules. From the value of the intensity ratios given in Table 1 it turns out that the concentration of T vs. H PEO is large, thus indicating that a non-negligible amount of H PEO has reacted to become T PEO when in contact with s-PMMA. This is especially true after the annealing process.

The model that emerges from the work of ref. 3 is based on a morphological study in which the detailed molecular structures lose their importance in favour of an overall description of how molecules may aggregate. On the contrary the message we obtain from vibrational spectroscopy is that the detailed molecular geometry of PEO is *trans* planar when in contact with s-PMMA. For a better understanding of what is really happening in the blend of PEO and s-PMMA, data from vibrational spectroscopy, SAXS and calorimetry should be accounted for with a unique model.

We recall that if the *trans* planar structure of s-PMMA is accepted as a working hypothesis, the repeat distance of the syndiotactic structure is approximately 4.8 Å, and thus two T PEO units may match three s-PMMA units. One could then write schematically the following reaction between monomeric units:



where the substance within square brackets is one 'mole' of the 'complex'. If this is the case, purely by consideration of the stoichiometry of the samples analysed in this work (weight ratio 3:1 PEO/PMMA), we should find an excess of unreacted PEO(H).

One can then reasonably assume that the 'unreacted' PEO(H) crystallizes into regular lamellae and that the fraction of 'reacted' PEO accommodates itself in contact with s-PMMA (or a-PMMA) necessarily in the interlamellar space. With this view our spectroscopic finding and the morphological data of refs. 2 and 3 are reconciled in a unique model. On this basis the intensity of the infra-red bands assigned to PEO(T) can be taken as a measure of the concentration of the material situated in the interlamellar spacing; i.r. then provides a direct and useful probe for the morphological characterization of these kinds of blends. More work is, however, needed for the definition of the absolute absorption coefficient of these new bands.

The description of the crystalline lamellae of PEO(H) embedded in the lamellar spacing where s-PMMA (or a-PMMA) interact with a sizeable fraction of PEO forcing it to become coplanar raises the interesting question on the origin of the phenomenon and on the kind of interaction forces which become active.

The problem that is opened by this work is how conformationally irregular s-PMMA (or a-PMMA) can force PEO to become planar. The problem is not limited to PEO/PMMA but has also been found by us at least

in the case of PEO and poly(vinyl acetate)<sup>13</sup>. This is a curious situation, which requires further consideration.

#### ACKNOWLEDGEMENTS

This work was partly supported by the Consiglio Nazionale delle Ricerche and by Fondi Ministeriali per la Ricerca. One of the authors (J.I.M.) is grateful to 'Programa de Estancias en el Extranjero' from Junta de Andalucia (Spain), which made possible his stay in Italy.

#### REFERENCES

- 1 Ramana Rao, G., Castiglioni, C., Gussoni, M., Zerbi, G. and Martuscelli, E. *Polymer* 1985, **26**, 811

- 2 Martuscelli, E., Canetti, M., Vicini, L. and Saves, A. *Polymer* 1982, **23**, 331
- 3 Silvestre, C., Cimmino, S., Martuscelli, E., Karasz, F. E. and MacKnight, W. J. *Polymer* 1987, **28**, 1190
- 4 Gussoni, M., Castiglioni, C. and Zerbi, G. *Chem. Phys. Lett.* 1983, **95**, 483; *J. Phys. Chem.* 1984, **88**, 600; *Chem. Phys. Lett.* 1983, **99**, 101
- 5 Miyazawa, T., Fukushiwa, K. and Ideguchi, Y. *J. Chem. Phys.* 1962, **37**, 2764
- 6 Yokoyama, M., Ochi, H., Tadokoro, H. and Price, C. C. *Macromolecules* 1972, **5**, 690
- 7 Takahashi, Y. and Tadokoro, H. *Macromolecules* 1973, **6**, 672
- 8 Takahashi, Y., Sumita, I. and Tadokoro, H. *J. Polym. Sci., Polym. Phys. Edn.* 1973, **11**, 2113
- 9 Tai, K. and Tadokoro, H. *Macromolecules* 1974, **7**, 507
- 10 Vacatello, M. and Flory, P. J. *Macromolecules* 1986, **19**, 405
- 11 Dybal, J., Stokr, J. and Schneider, B. *Polymer* 1983, **24**, 971
- 12 Kusanagi, H., Tadokoro, H. and Chatani, Y. *Macromolecules* 1976, **9**, 531
- 13 Orlandi, E. Thesis, University of Milano, 1986