Compatibility and crystallization of tetrahydrofuran–methyl methacrylate diblock copolymer/polytetrahydrofuran blends

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The compatibility and crystallization of tetrahydrofuran–methyl methacrylate diblock copolymer (PTHF-*b*-PMMA)/tetrahydrofuran homopolymer (PTHF) blends were studied. Our results showed that the crystallization and morphology of compatible PTHF-*b*-PMMA/PTHF blends are very different from those of incompatible blends. The compatibility of the blends was successfully and very conveniently determined by analysing their crystallization behaviour, and the result is in good agreement with the compatibility determined by direct observation under an optical microscope. Some very unusual crystalline morphologies were discovered for the compatible PTHF-*b*-PMMA/PTHF blends resulting from the effect of PMMA microdomains in the blends.

(Keywords: block copolymer; blends; compatibility)

INTRODUCTION

A number of theoretical and experimental studies[1-11] have appeared in the literature regarding the compatibility and microphase separation of mixtures of block copolymer with homopolymer, and there are also many published reports[12-28] about the crystallization, structure and morphology of crystalline block copolymers. This has made it possible to explore the compatibility and crystallization of crystallizable mixtures of block copolymer with homopolymer, and there have been a few reports about this study[29-31].

In recent years, we have studied the compatibility, crystallization and morphology of the mixtures of block copolymer with homopolymer[31-37]; they are usually very different from both the copolymer and the homopolymer in many respects. In the present work, we studied mixtures of tetrahydrofuran–methyl methacrylate diblock copolymer (PTHF-*b*-PMMA) with tetrahydrofuran homopolymer (PTHF). We found that the compatibility of the blends (the solubility of PTHF homopolymer in the PTHF domain of the blends) could be very conveniently determined from their crystallization thermograms. Some very unusual crystalline morphologies were discovered for compatible PTHF-*b*-PMMA/PTHF blends.

EXPERIMENTAL

Preparation of the copolymer

Details of the synthesis of PTHF-*b*-PMMA were reported previously. In brief, the copolymer was synthesized in the laboratory by a novel route of cationic to anionic mechanism transformation. The PTHF prepolymers, which are also used as the homopolymer component in our blends, were synthesized by a cationic ring-opening mechanism. THF polymerization was initiated by adding benzyl bromide to a well-stirred solution of silver perchlorate hydrate in THF monomer at 258 K; the reaction was allowed to proceed for about 40 h. This polymerization was finally terminated by addition of aniline. The PTHF-*b*-PMMA diblock copolymer was obtained by adding sodium naplithalen to THF and methyl methacrylate monomer (MMA) solution of the purified PTHF prepolymer. The copolymerization was allowed to proceed for about 16 h at room temperature and then terminated by pouring the reaction product into a 0.1 molar solution of HCl in distilled water. Purification of the block copolymers was carried out in order to free them from a small amount of unwanted homopolymer. PTHF homopolymer was removed by precipitating the products three times from acetone solution into a large excess of petroleum ether; the homo-PMMA still remaining in the products was removed by crystallization of the PTHF block of the copolymer in acetone solution at 253 K. In this way, very pure PTHF-*b*-PMMA diblock copolymers were obtained.

Molecular characterization of polymers

A summary of the synthesized PMMA-*b*-PTHF diblock copolymer is given in *Table 1*. The composition of the copolymer was determined by proton n.m.r. The molecular weights of PTHF-*b*-PMMA diblock copolymer and PTHF homopolymers were measured by membrane osmometry at 333.2 K in benzene.

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Table 1 Characterization of PTHF-*b*-PMMA diblock copolymer

M_n	Weight fraction of PTHF block	M_w/M_n
21 000	0.52	1.99

Table 2 Designation of the blends

Designation	Weight fraction of PTHF-*b*-PMMA	M_n (PTHF)
L10	1.0	2 000
L9	0.9	2 000
L8	0.8	2 000
L7	0.7	2 000
L6	0.6	2 000
L5	0.5	2 000
L4	0.4	2 000
L3	0.3	2 000
L2	0.2	2 000
L1	0.1	2 000
L0	0.0	2 000
H9	0.9	13 000
H8	0.8	13 000
H7	0.7	13 000
H0	0.0	13 000

Preparation of blends

The PTHF-*b*-PMMA/PTHF blends were prepared by solution casting from chloroform, a non-preferential solvent for both blocks of the copolymer. The cast films were placed in a vacuum for a week at room temperature in order to remove residual solvent. Designations of the blends are given in *Table 2.*

Differential scanning calorimetry (d.s.c.)

A Perkin–Elmer DSC-2c differential scanning calorimeter was used to study the crystallization of PTHF-*b*-PMMA/PTHF blends. The d.s.c. cooling thermograms were obtained at a rate of $-10\,\mathrm{K\,min^{-1}}$ after the samples were tempered for 10 min at 383 K, and then the melting thermograms were obtained at a heating rate of $10\,\mathrm{K\,min^{-1}}$.

Polarized optical microscopy

A polarized optical microscope was used to study the crystalline morphology of the blends. The samples were cast from chloroform and then isothermally crystallized at 288 K. Micrographs of the spherulites of the blends were taken with a 35 mm camera.

RESULTS AND DISCUSSION

Crystallization and compatibility

It is known that the phase separation behaviour is very different for compatible and incompatible amorphous mixtures of block copolymer with homopolymer. A similar situation could be expected for compatible and incompatible crystallizable mixtures of block copolymer with homopolymer in the melt. Therefore, the crystallization behaviour of such compatible and incompatible blends could be very different, and there could also be some relationship between the crystallization and compatibility.

*Crystallization of compatible PTHF-*b*-PMMA/PTHF blends.* The L series of blends (*Table 2*) are all transparent in the melt, and homogeneous under direct observation by optical microscope, indicating that all the blends are macroscopically compatible in the melt. This good compatibility of the L series of blends resulted from the much lower molecular weight of the PTHF homopolymer than that of the PTHF block of the copolymer. For these compatible blends, our d.s.c. studies showed that only one crystallization peak (T_c) was detected during cooling and one melting peak (T_m) was observed during melting. The curves of T_c and T_m *versus* blend composition are shown in *Figures 1* and *2*, respectively. From *Figure 1* it is seen that the crystallization temperature (T_c) increases rapidly with increase of PTHF homopolymer weight fraction when this fraction is less than 0.5, indicating that the PTHF microdomains could crystallize much faster when they were swollen by PTHF homopolymer. The melting points (T_m) of the blends increase at first and then

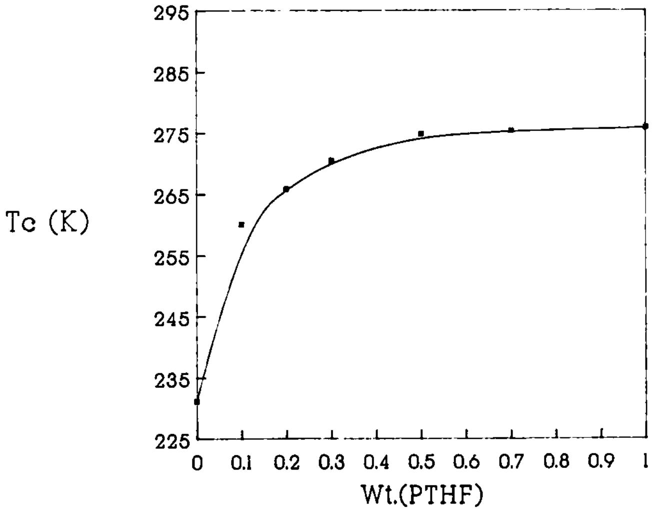


Figure 1 The crystalline temperature (T_c) of the L series of PTHF-*b*-PMMA/PTHF blends during d.s.c. cooling at a rate of $-10\,\mathrm{K\,min^{-1}}$

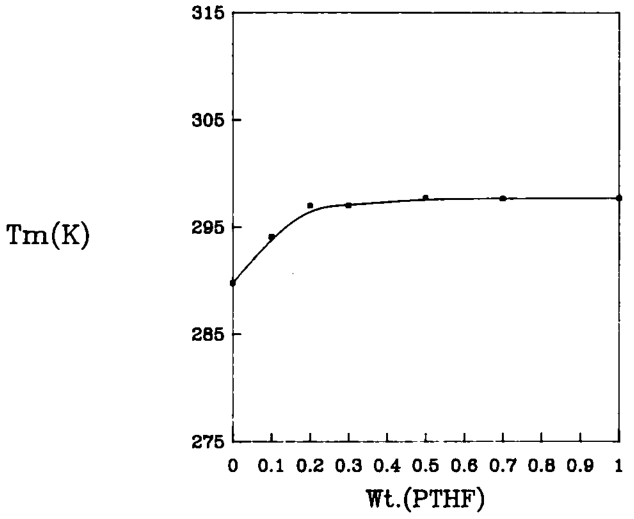


Figure 2 The melting point (T_m) of the L series of PTHF-*b*-PMMA/PTHF blends at a heating rate of $10\,\mathrm{K\,min^{-1}}$ after the samples were cooled down to 213 K at a rate of $-10\,\mathrm{K\,min^{-1}}$

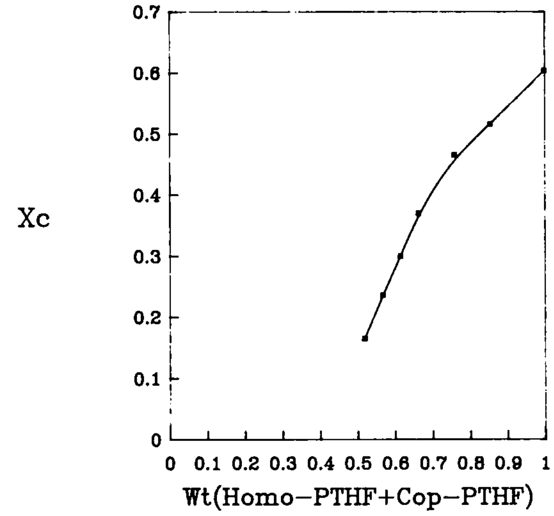


Figure 3 The crystallinity (X_c) of the PTHF phase of the L series of PTHF-*b*-PMMA/PTHF blends, calculated from the melting process

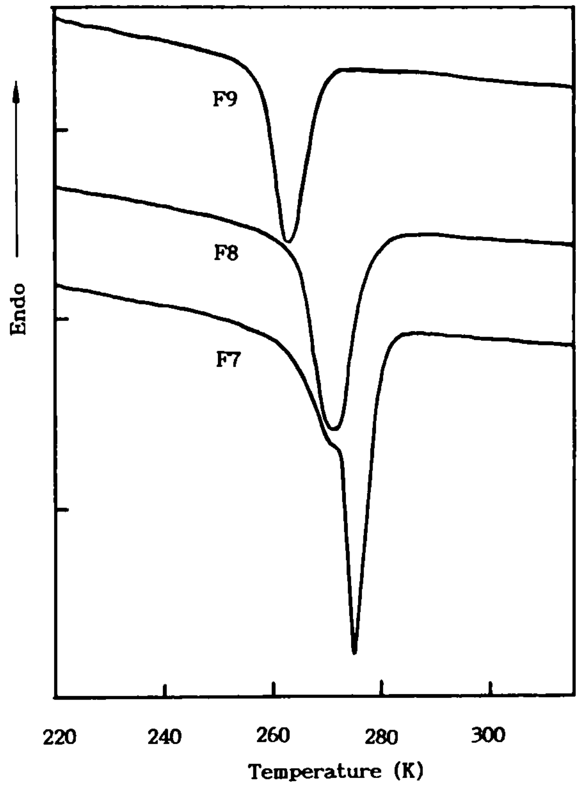


Figure 4 D.s.c. cooling ($-10\ \mathrm{K\ min^{-1}}$) thermograms of the F series of PTHF-*b*-PMMA/PTHF blends

remain constant with increase of PTHF homopolymer weight fraction (*Figure 2*). *Figure 3* gives the crystallinity (X_c) curve of the PTHF phase of the blends *versus* the THF weight fraction (including PTHF block of the copolymer and PTHF homopolymer). The crystallinity (X_c) also increases with increase in the PTHF homopolymer fraction, indicating that the more PTHF homopolymer in the PTHF microdomains, the higher the X_c of the PTHF phase. But unlike the T_c and T_m of the blends, the X_c of any blend studied is always smaller than that of the pure PTHF homopolymer sample. This implies that no matter how much PTHF homopolymer the blends contain, the crystallinity of the PTHF block of the copolymer can never reach the crystallinity of the pure PTHF homopolymer sample, although the addition of PTHF homopolymer could give the PTHF block of the copolymer a more favourable conformation and therefore a slightly improved crystallization ability.

Determination of compatibility degree from crystallization. The compatibility of amorphous mixtures of diblock copolymer with its corresponding homopolymer is strongly dependent on the molecular weight ratio of the homopolymer to its corresponding block of the copolymer. Therefore, the compatibility of PTHF-*b*-PMMA/PTHF blends can be easily changed by varying the molecular weight of PTHF homopolymer, and the effect of the compatibility of block copolymer/homopolymer blends on their crystallization and morphology could be very different with the homopolymer blends owing to the existence of microphase separation in the former blends. In the present work, another series (F series) of PTHF-*b*-PMMA/PTHF blends (see *Table 2*) was also studied; the only difference between these blends and the L series of blends is that the molecular weight of the PTHF homopolymer in the F series is a little higher than that of the PTHF block of the copolymer, which could lead to a large difference in compatibility between the F and the L series of blends.

Direct observation by optical microscopy showed that sample H9, with 10% of PTHF homopolymer, is macroscopically homogeneous in the melt, and samples H8 and H7, with PTHF homopolymer weight fractions of 0.2 and 0.3, respectively, are macroscopically phase-separated. Because of the differences in

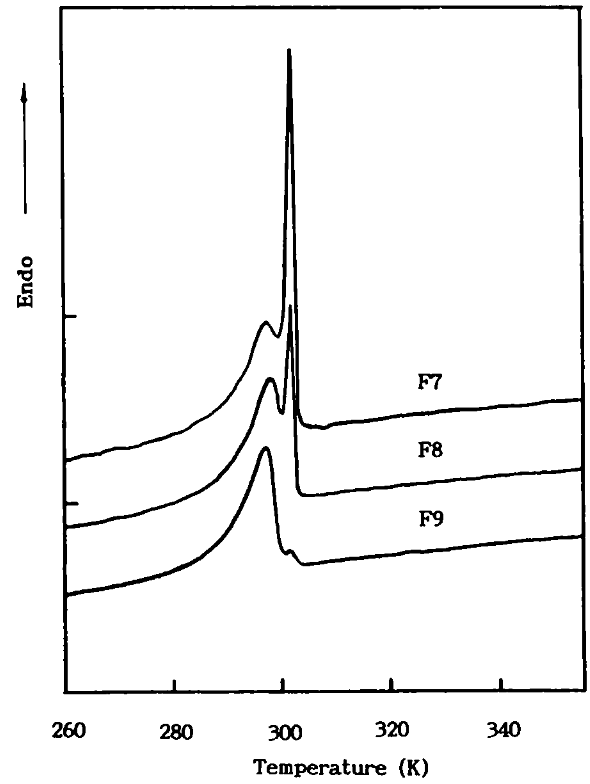
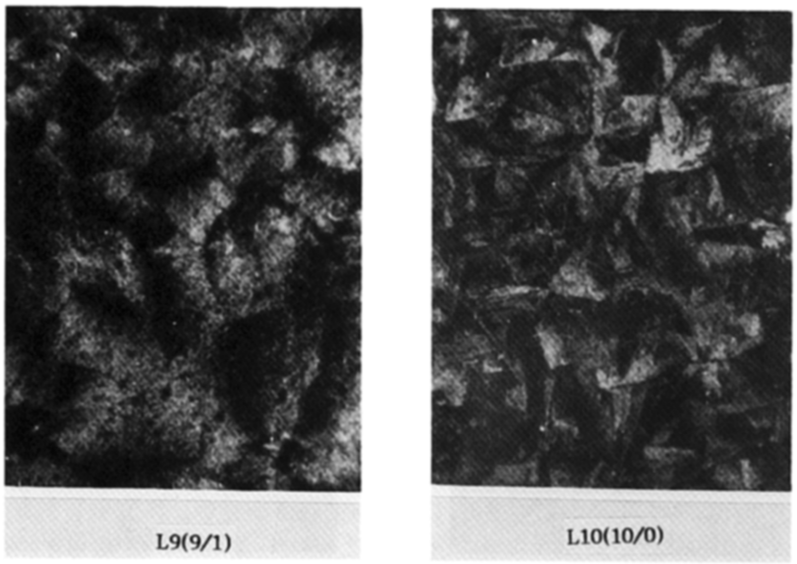


Figure 5 D.s.c. melting ($10\ \mathrm{K\ min^{-1}}$) thermograms of the F series of PTHF-*b*-PMMA/PTHF blends after the samples were cooled down to 213 K at a rate of $-10\ \mathrm{K\ min^{-1}}$


L0(0/10)
L1(1/9)
L2(2/8)
L3(3/7)
L4(4/6)
L5(5/5)
L6(6/4)
L7(7/3)
L8(8/2)

Figure 6 Optical micrographs of the L series of compatible PTHF-*b*-PMMA/PTHF blends cast from chloroform and isothermally crystallized at 288 K (magnification 910 ×)



L9(9/1)

L10(10/0)

Figure 6 *continued*

compatibility, different crystallization behaviour could be expected. During the cooling process, two crystalline peaks (one of them is not very clear owing to the overlap of the peaks) were observed when the PTHF weight fraction reached 0.3 (sample H7), as shown in *Figure 4*, and two very clear melting peaks were observed for all the blends in the melting process (*Figure 5*), although the higher T_m peak of sample H9 is very small.

Since the melting point (T_m) of the PTHF homopolymer is much higher than that of PTHF microdomains of pure PTHF-*b*-PMMA diblock copolymer, the higher melting point of the F series of blends in *Figure 2* is the contribution of the homo-PTHF macroscopic phase of the blends. The fact that the higher melting peak gets larger and larger with increase of PTHF homopolymer fraction also provides evidence to support the above conclusion. The lower T_m is therefore the contribution of PTHF microdomains of the copolymer swollen by some PTHF homopolymer molecules. That is, there is only one melting point for compatible PTHF-*b*-PMMA/PTHF blends (such as the L series of blends), and there are two melting points for incompatible PTHF-*b*-PMMA/PTHF blends.

Because the higher T_m peak of sample H9 is really very small, it could be assumed that this sample is more or less compatible; that is, for the F series of blends, the solubility of PTHF homopolymer in PTHF microdomains of the copolymer is only about 10%. The compatibility results of the PTHF-*b*-PMMA/PTHF blends, obtained from the analysis of their d.s.c. thermograms, were in good agreement with the conclusion drawn from direct optical microscopic observation. This shows that the compatibility of PTHF-*b*-PMMA/PTHF blends can be easily determined by simply analysing their d.s.c. crystallization behaviour.

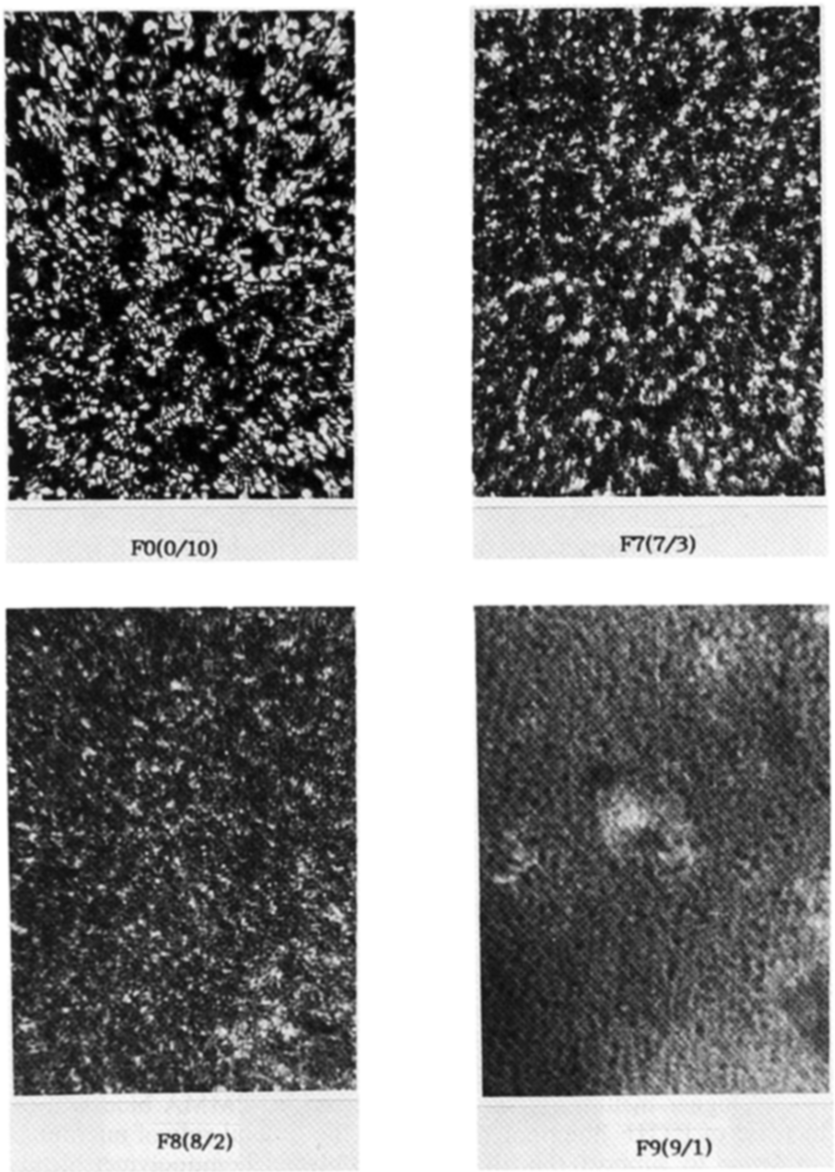
Unusual crystalline morphologies of compatible PTHF-b-*PMMA/PTHF blends*

As shown in *Figure 6*, some crystalline morphologies of the compatible PTHF-*b*-PMMA/PTHF blends, cast from solvent and crystallized at 288 K, are very unusual; the crystalline morphologies of the blends also changed greatly with blend composition. Such unusual crystalline morphologies and the strong dependence of morphology on blend composition have not previously been reported in the literature for compatible amorphous/semicrystalline homopolymer blends. The interesting morphologies can only result from the effect of microphase separation.

Because the major component of the copolymer used in this study is PTHF, the PTHF components (including PTHF homopolymer and PTHF block of the copolymer) of the blends are major components for all the blends. The dispersed microdomains in the melt were therefore formed by PMMA blocks of the copolymer, according to the general rule of microphase separation of diblock copolymer/homopolymer blends. It is such amorphous, hard PMMA microdomains dispersed (at least in the melt) in these compatible blends that play an important role in the formation of the unusual crystalline morphologies. It is known that spherical, cylindrical, lamellar and OBDD microdomain morphologies can be formed in amorphous blends of a diblock copolymer AB and its corresponding homopolymer A with a change in blend composition. Therefore, the different spherulite morphologies of the PTHF-*b*-PMMA/PTHF blends probably result partly from different microphase separation morphology.

The crystalline morphologies of the F series of PTHF-*b*-PMMA/PTHF blends, as shown in *Figure 7*, do not change as much as those of the L series owing to their poor compatibility. The PTHF homopolymer (sample H0) of higher molecular weight ($M_n = 13\,000$) forms well organized spherulites. The spherulitic morphology of the incompatible blends F7 and F8 is disturbed by the macrophase separation of the blends. For the approximately compatible blend F9, where the PTHF homopolymer weight fraction is only 0.1, only a few crystallized particles are observed because most of the homopolymer stays and crystallizes in PTHF microdomains.

From the above results, we can draw the following



F0(0/10)

F7(7/3)

F8(8/2)

F9(9/1)

Figure 7 Optical micrographs of the F series of PTHF-*b*-PMMA/PTHF blends cast from chloroform and isothermally crystallized at 288 K (magnification 910 ×)

conclusions for crystallizable mixtures of block copolymer with homopolymer: (1) unusual crystalline morphologies can be expected owing to the existence of microdomains of block copolymer; (2) the compatibility degree can be determined by simply analysing the d.s.c. melting behaviour.

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