Crystallization of poly(ethylene oxide) in a mixture with poly(methyl methacrylate) under high pressure

C. Nakafuku and N. Toyonaga
Faculty of Education, Kochi University, Kochi 780, Japan
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The effects of mixing with poly(methyl methacrylate) (PMMA) on the melting and crystallization process of poly(ethylene oxide) (PEO) were studied under high pressures up to 500 MPa by d.t.a. The intensity of the X-ray diffraction peak of PEO in the sample crystallized at 500 MPa was compared with the intensity of the sample crystallized at 0.1 MPa. Melting point (T_m) depression of PEO observed at 0.1 MPa with decreasing PEO in the mixture was almost constant up to 500 MPa. The depression rate of the crystallization temperature (T_c) of PEO with PMMA content decreased at elevated pressures up to 500 MPa. The intensity of the exothermic peak of crystallization of PEO in the d.t.a. curve of the sample of medium PEO content increased with pressure. The intensity of the wide-angle X-ray diffraction line of PEO in the sample crystallized at 500 MPa was larger than that of the sample crystallized at 0.1 MPa. Optical microscopic observation of the high pressure crystallized lower PEO content blend showed partial spherulite formation, indicating increased crystallizability at elevated pressure.

(Keywords: poly(ethylene oxide); poly(methyl methacrylate); binary mixture; high pressure; melting; d.t.a.; crystallization; phase diagram; X-ray)

INTRODUCTION

In the past decade, many investigations on the compatibility of poly(ethylene oxide) (PEO) and poly(methyl methacrylate) (PMMA) have been reported. According to Cortazar *et al.*[1], melting point (T_m) depression of PEO occurred with increasing PMMA in the binary mixture and the calculated interaction parameter was negative, indicating miscibility between the two polymer molecules in the melt. Calahorra *et al.* showed that the crystallization process of PEO was affected by mixing with PMMA[2,3]. Martuscelli *et al.* studied the compatibility of a PEO/PMMA binary mixture using wide-angle X-ray scattering[4] and ^{13}C n.m.r.[5]. They also reported that the growth process of PEO crystals is complicated by mixing with PMMA molecules. Reduction of the mobility of the PEO chain occurred due to the presence of the amorphous PMMA molecules[6]. Ramana Rao *et al.* studied the blend film of PEO and PMMA by Fourier transform infra-red spectra[7]. They concluded that the molecules of PEO and PMMA were completely miscible in the melt but the intermolecular interactions between the two molecules were weak and the interactions were not chemical but physical. A single glass transition temperature was reported in the d.s.c. measurement for this binary mixture, indicating miscibility of the two components in the amorphous phase[8].

The effect of pressure on the melting and crystallization of crystalline polymers in a binary mixture with amorphous polymer has recently been studied. In the miscible blend of poly(vinylidene fluoride) (PVDF) and PMMA, the crystallization of PVDF was impeded by PMMA molecules with increasing pressure[9]. Crystallization of poly(ε-caprolactone) (PCL) was also impeded under high pressure by a miscible copolymer, poly(styrene-*co*-acrylonitrile) (SAN)[10]. The depression rate of the crystallization temperature (T_c) of PCL with SAN content increased at elevated pressure.

In this paper, the effects of pressure on the melting and crystallization behaviour of the PEO molecule in a mixture with PMMA were studied. The change of depression rate of T_m and T_c of PEO with increasing PMMA was determined at elevated pressure and compared with that of T_m and T_c of PCL, which forms a completely miscible blend with SAN with an acrylonitrile content of 25 wt%. The change in the X-ray diffraction intensity with PEO content was measured for PEO/PMMA samples crystallized at 0.1 MPa and 500 MPa. Polarized microscopic observation was also performed for the blend samples crystallized at 0.1 MPa and 500 MPa.

EXPERIMENTAL

A PEO sample with a molecular weight of 200 000 was purchased from Scientific Polymer Products, Inc. A PMMA sample with a molecular weight of 93 300 was purchased from the same company. The mixed powder (0.4 g) of PEO and PMMA with a desired weight fraction of PEO (W_{PEO}) was dissolved in 80 ml of 1,2-dichloroethane at room temperature in a laboratory dish and the solvent was evaporated at 25°C for 2 days. The film sample was completely dried in a vacuum oven. The blend film obtained was cut into small pieces and a rod-like sample, 1.8 mm in diameter, was moulded in a

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glass tube at 130°C. After cooling to room temperature (cooling rate 24°C min^{-1}), the rod-like sample was pushed out from the glass tube.

D.t.a. was performed under high pressure using apparatus described elsewhere[9]. A small pellet-like sample (1.8 mm in diameter and 1.8 mm in length) cut from the rod was wrapped in aluminium foil and attached to the thermocouple junction of the differential thermal anlyser. In the d.t.a. experiment, the heating rate was 5 K min^{-1} and the cooling rate was about 4–5 K min^{-1}. Run 1 in d.t.a. is the melting process of the sample cut from the rod and run 2 is the crystallization process by slow cooling (4–5 K min^{-1}). Run 3 is the melting of the sample crystallized through run 2. A difference was observed in the melting peak position and intensity between run 1 and run 3, especially for lower content of PEO.

The samples for X-ray diffraction measurement were formed into a sheet (1 mm thick, 2.5 mm wide and 17 mm long) using a brass mould. These samples were covered with aluminium foil and epoxy resin and crystallized at 0.1 MPa and at 500 MPa by slowing cooling from the fused state (12–15°C higher temperature than the peak melting temperature) at the same cooling rate as that of d.t.a.

The sample for optical microscopic observation was prepared as follows. A solution of the PEO/PMMA mixture of desired W_{PEO} was dropped onto the cut slide glass (7 mm wide and 26 mm long) and a thin film sample was obtained by evaporating the solvent for 24 h. The sample with the slide glass was covered by aluminium foil and epoxy resin. High pressure crystallization of the sample was performed by the same process as the sample preparation for X-ray measurements.

RESULTS AND DISCUSSION

Figures 1 and *2* show the d.t.a. melting curve (run 1) and crystallization curve, respectively, at 0.1 MPa of pure PEO and PEO in the mixture. The endothermic peak of melting shifted to the low temperature side very slightly and the peak intensity decreased with decreasing PEO content down to $W_{\mathrm{PEO}} = 0.3$. The peak of melting still appeared at $W_{\mathrm{PEO}} = 0.3$ in run 1 but it disappeared in run 2 (crystallization process) and run 3 (re-melting process). The peak intensity of crystallization also decreased with decreasing PEO content in the mixture. *Figure 3* shows the change in peak melting temperature (T_{m}) in run 1 and T_{c} in run 2 with PEO content at 0.1 MPa. Both T_{m} and T_{c} of PEO decreased with W_{PEO} and the rate of decrease of T_{c} was much larger than that of T_{m}.

Figure 4 shows the d.t.a. curve of melting and crystallization of pure PEO at elevated pressure. The endothermic peak of melting and the exothermic peak of crystallization shifted to the high temperature side with increasing pressure but the shape and intensity of the peak did not change with pressure. *Figure 5* shows the d.t.a. curve of melting and crystallization of PEO in the mixture with $W_{\mathrm{PEO}} = 0.6$ at elevated pressure. The peak shifted to the high temperature side with pressure in the same way as for pure PEO. The intensity of the melting peak decreased with pressure but the intensity of the crystallization peak increased with pressure.

High pressure d.t.a. was performed for the blend sample with $W_{\mathrm{PEO}} = 1.0$–0.5. In $W_{\mathrm{PEO}} = 0.4$ and 0.3, a

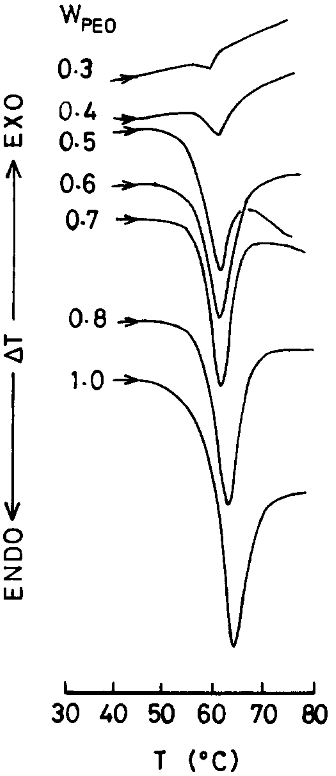

Figure 1 D.t.a. melting curve of PEO in the mixture with PMMA at 0.1 MPa

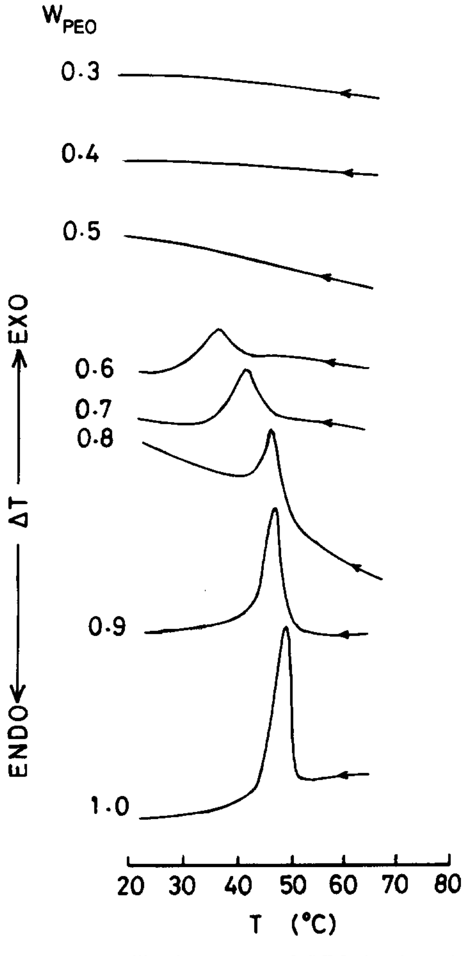

Figure 2 D.t.a. crystallization curve of PEO in the mixture with PMMA at 0.1 MPa

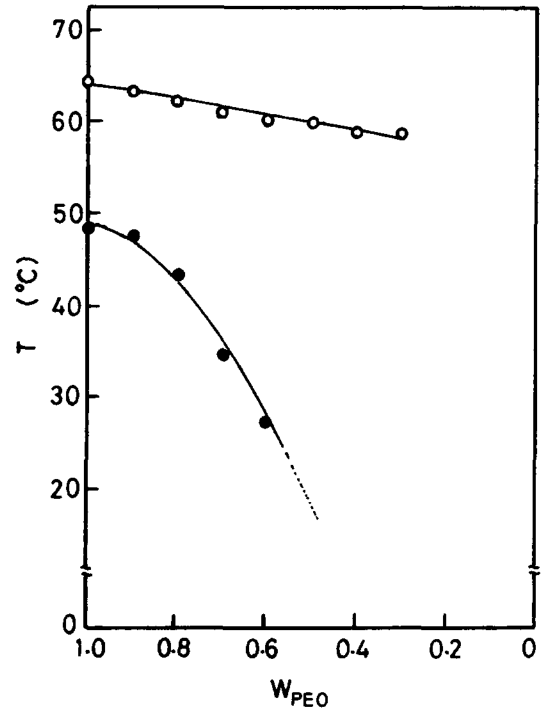

Figure 3 Change of the melting and crystallization temperature of PEO with W_{PEO}. ○, T_m; ●, T_c

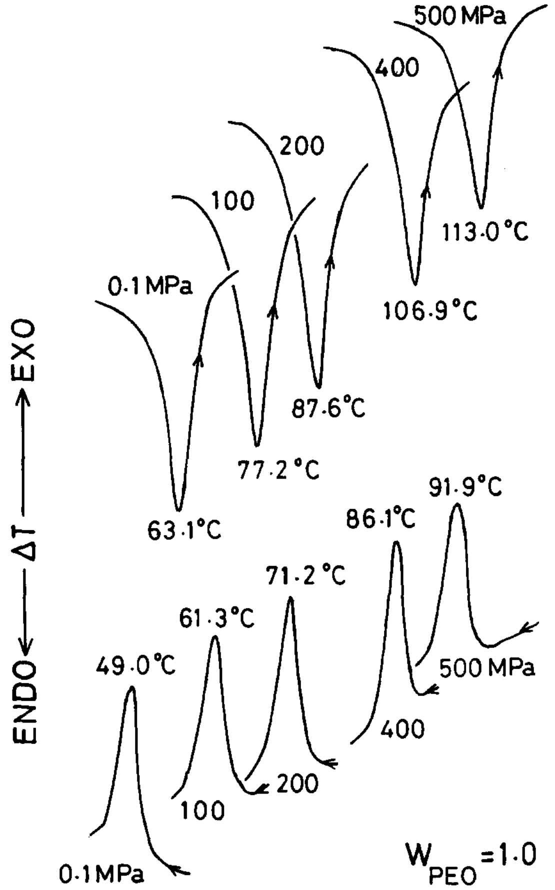

Figure 4 D.t.a. melting and crystallization curves of pure PEO at elevated pressure

small peak of melting appeared only in run 1 at 0.1 MPa and no peak of melting was observed in run 3 at 0.1 MPa and under high pressure.

Pressure dependence of T_m and T_c of PEO in the mixture with $W_{PEO} = 0.6$ and pure PEO up to 500 MPa is shown in *Figure 6*. It is clearly seen that the melting curve (T_m *versus* pressure) of $W_{PEO} = 0.6$ shifts almost parallel to the low temperature side, but the pressure dependence (inclination of the curve at 0.1 MPa) of the

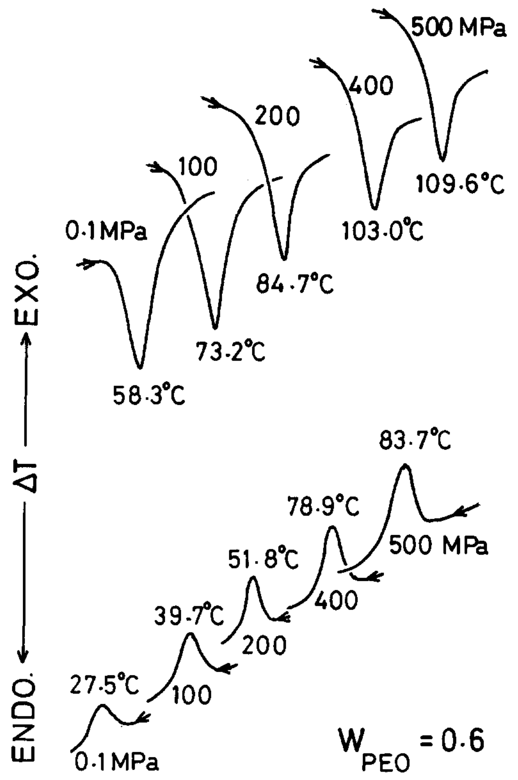

Figure 5 D.t.a. melting and crystallization curves of PEO in the mixture with $W_{PEO} = 0.6$ at elevated pressure

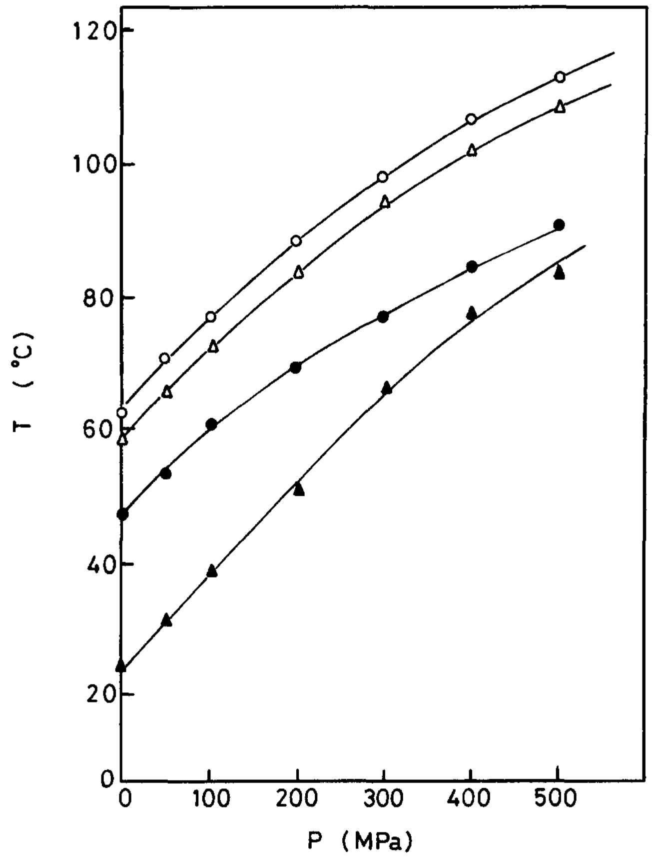

Figure 6 Pressure dependence of T_m and T_c of pure PEO and PEO in the mixture with $W_{PEO} = 0.6$. ○, T_m of pure PEO; △, T_m of PEO with $W_{PEO} = 0.6$; ●, T_c of pure PEO; ▲, T_c of PEO with $W_{PEO} = 0.6$

Table 1 Values of A, B and C in the equation, $T_m = A + BP - CP^2$, for the melting temperature of PEO in the mixture with different weight fractions in d.t.a.

W_{PEO}	A (°C)	B (K MPa^{-1})	$C \times 10^{-5}$ (K MPa^{-2})
1.0	63.8	0.142	8.62
0.9	63.5	0.141	8.87
0.8	62.9	0.141	8.90
0.7	60.3	0.142	8.33
0.6	59.6	0.143	8.59
0.5	59.5	0.140	8.12

Table 2 A', B' and C' in the equation, $T_c = A' + B'P - C'P^2$, for the crystallization temperature of PEO in the mixture with different weight fractions in d.t.a.

W_{PEO}	A' (°C)	B' (K MPa^{-1})	$C' \times 10^{-5}$ (K MPa^{-2})
1.0	49.5	0.123	7.73
0.9	47.7	0.123	7.69
0.8	43.5	0.124	6.60
0.7	34.9	0.155	10.25
0.6	25.1	0.171	10.08
0.5[a]	20.0	0.194	14.04

[a] Values determined using experimental data above 200 MPa where exothermic peak of crystallization appears

crystallization curve in the sample of $W_{PEO} = 0.6$ is larger than that of the sample of pure PEO. The inclination increased systematically with decreasing PEO content in the mixture. The melting and crystallization curves fit the quadratic equation

$$T_m, T_c = A + BP - CP^2$$

and the coefficients A, B and C were determined by the least squares method. The value of A is approximately equal to T_m and the value of B is approximately equal to the pressure dependence of T_m (dT_m/dP). The pressure coefficient of the melting temperature (dT_m/dP) of pure PEO ($W_{PEO} = 1.0$) determined by the coefficient B of P in the quadratic equation was 0.142 K MPa^{-1}. For all the samples with $W_{PEO} = 1.0$–0.5, the data were fitted to the quadratic equation and the coefficients A, B and C for the melting and A', B' and C' for the crystallization are listed in *Tables 1* and *2*, respectively. The tables show that T_m of PEO (A) in the mixture decreased with decreasing PEO content but the pressure coefficients of T_m (B) did not change within experimental error. On the contrary, the pressure coefficient of T_c (B') increased with decreasing PEO content.

Values of T_m and T_c were determined at 100 MPa intervals up to 500 MPa by using the values of *Tables 1* and *2* and the quadratic equation. The changes of T_m and T_c with the W_{PEO} at 300 MPa and 500 MPa are shown in *Figure 7*. The rate of decrease of T_m with PEO content did not change with pressure up to 500 MPa. However, the rate of decrease of T_c at 0.1 MPa was very large, as observed in *Figure 3*, and T_c decreased at elevated pressure. The temperature difference of T_c between $W_{PEO} = 1.0$ and 0.6 was about 24°C at 0.1 MPa but the difference was about 10°C at 500 MPa. This indicates that the crystallization of PEO in the mixture with PMMA is accelerated at elevated pressure. The increase in the peak intensity of the d.t.a. crystallization curve of PEO in the mixture with $W_{PEO} = 0.6$ (*Figure 5*) also suggests increased crystallizability of the PEO molecules at high pressure compared with the crystallizability at 0.1 MPa in the mixture.

The exothermic peak of crystallization of PEO was observed to appear at elevated pressure in the mixture with decreased PEO content, although no peak was observed at 0.1 MPa. In the mixture with $W_{PEO} = 0.5$, the peak of crystallization began to appear at 300 MPa but with $W_{PEO} = 0.3$, the peak was observed only at 500 MPa, as shown in *Figure 8*. In *Figure 8*, runs 1, 2 and 3 are the same process as described in the Experimental section. Run 4 is the melting process at 500 MPa of the sample crystallized at 0.1 MPa so that no peak of melting appeared. Run 5 is the crystallization process at the same pressure. An exothermic peak of crystallization is observed at this pressure. A small endothermic peak of melting appeared on the high pressure crystallized sample, indicating the existence of PEO crystals. In the series of experiments in *Figure 8*, it is concluded that crystallization of PEO by slow cooling at 500 MPa in the mixture with PMMA occurs easily compared with crystallization by slow cooling at 0.1 MPa.

Polarized microscopic observation also supports the above reasoning. *Figures 9a* and *b* show micrographs of the PEO/PMMA blend with $W_{PEO} = 0.3$ crystallized at 0.1 MPa and 500 MPa, respectively. It is clear that partial spherulite formation occurs in the sample crystallized at 500 MPa but the sample cryallized at 0.1 MPa shows no crystalline phase. In the microscopic observation of the series of samples with $W_{PEO} = 1.0$–0.3, formation of spherulites is evident for the sample crystallized at 500 MPa, but the sample crystallized at 0.1 MPa did not show spherulites below $W_{PEO} = 0.5$.

In order to substantiate the above remarks, wide angle X-ray diffraction measurement was performed for the

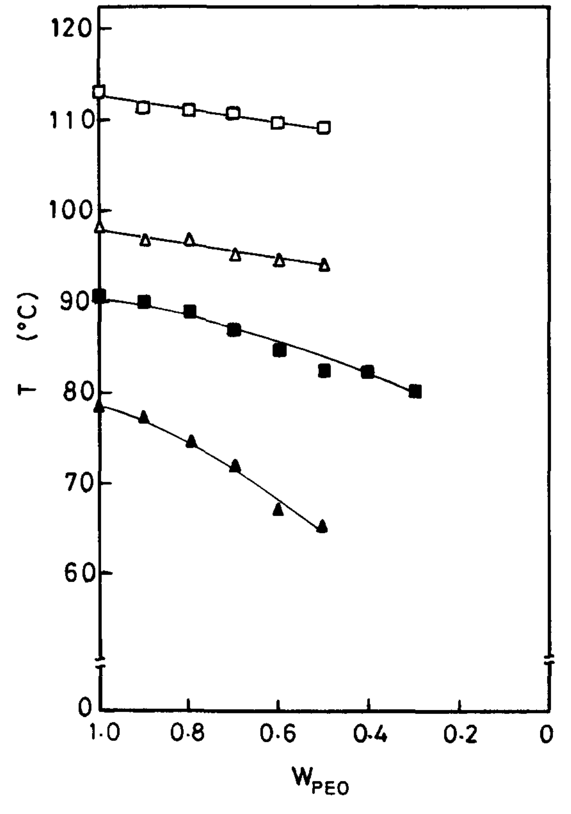

Figure 7 Phase diagram of melting and crystallization of PEO in the mixture under high pressure. △, Melting at 300 MPa; □, melting at 500 MPa; ▲, crystallization at 300 MPa; ■, crystallization at 500 MPa

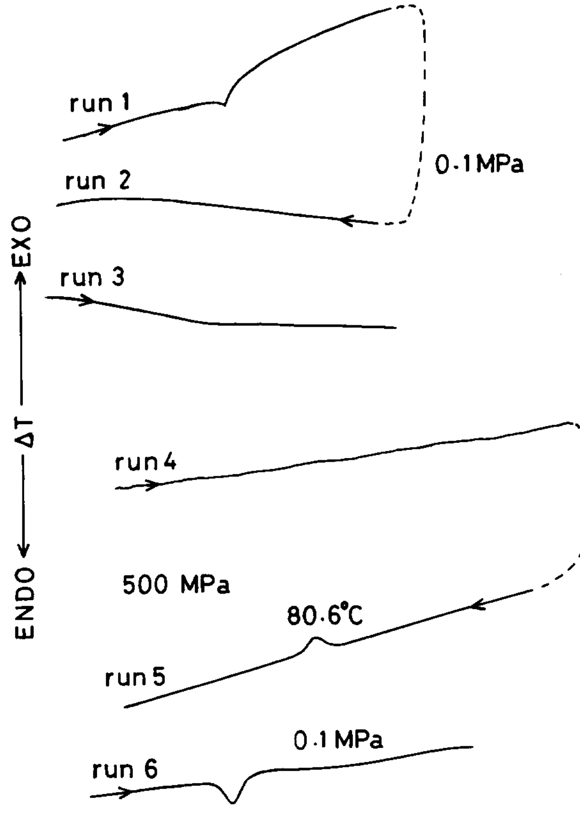

Figure 8 D.t.a. curve of melting and crystallization of PEO in the mixture with $W_{PEO} = 0.3$. Runs 1, 2 and 3 represent the d.t.a. curve at 0.1 MPa and runs 4 and 5 at 500 MPa. Run 6 is the melting curve of d.t.a at 0.1 MPa on the sample crystallized at 500 MPa

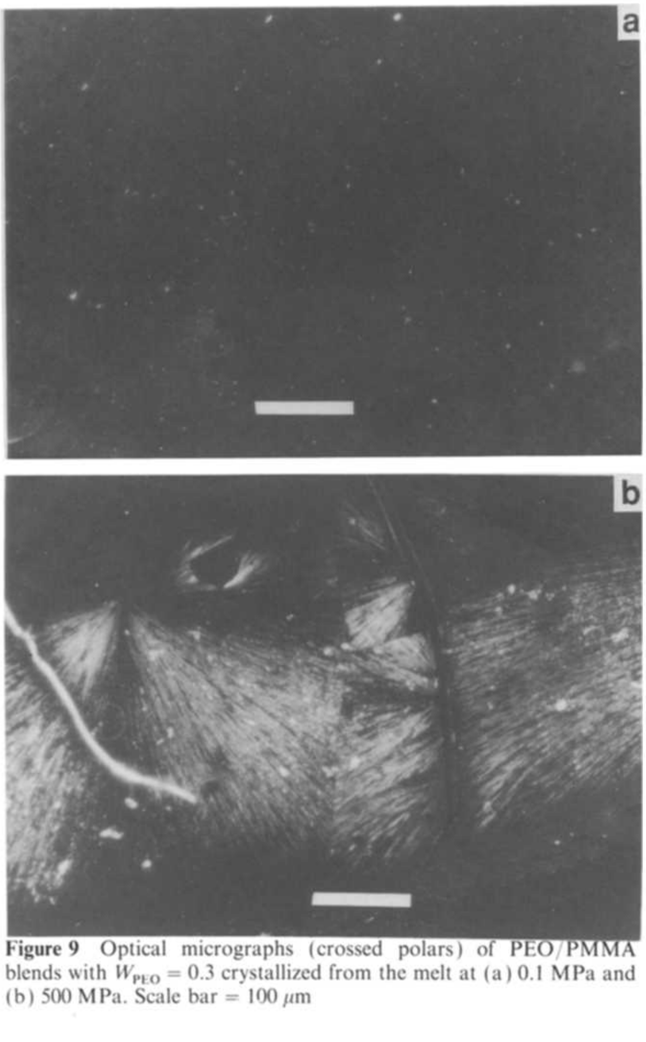

Figure 9 Optical micrographs (crossed polars) of PEO/PMMA blends with $W_{PEO} = 0.3$ crystallized from the melt at (a) 0.1 MPa and (b) 500 MPa. Scale bar = 100 μm

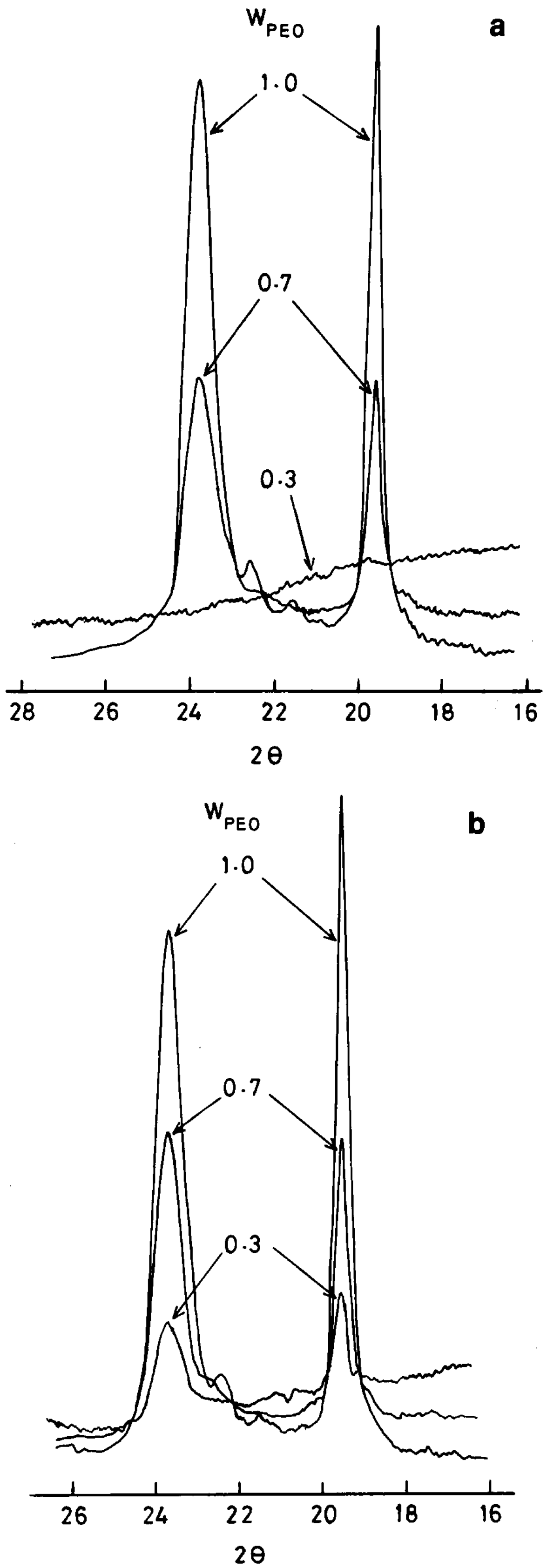

Figure 10 X-ray diffraction pattern of pure PEO and PEO in the mixture with $W_{PEO} = 0.7$ and 0.3, crystallized at (a) 0.1 MPa and (b) 500 MPa

mixed sample with different W_{PEO} values crystallized at 0.1 MPa and 500 MPa. *Figures 10a* and *b* show the X-ray diffraction patterns of PEO in the mixtures with $W_{PEO} = 1.0, 0.7$ and 0.3, between $2\theta = 16°$ and $28°$, for the samples crystallized at 0.1 MPa and 500 MPa, respectively. The

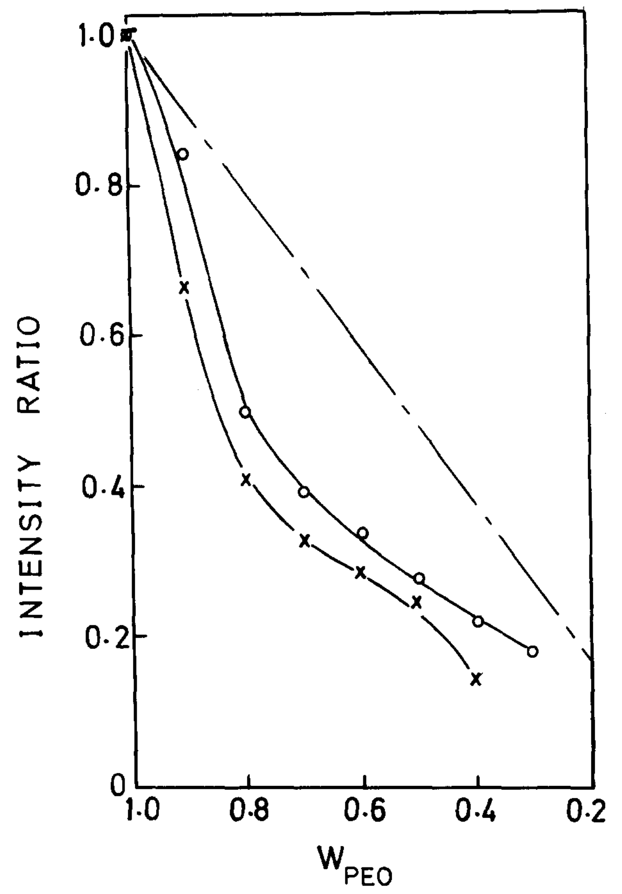

Figure 11 Peak intensity ratio of (1 2 0) line of PEO in the mixture with pure PEO plotted against W_{PEO}. ×, Crystallized at 0.1 MPa; ○, crystallized at 500 MPa; — — — — —, line drawn assuming no interaction

intensity of the (1 2 0) and (1 1 2) diffraction peaks from PEO decreased with decreasing PEO content and the diffraction peak disappeared at $W_{PEO} = 0.3$ for the sample crystallized at 0.1 MPa; however, for the sample crystallized at 500 MPa, the diffraction peak still exists at $W_{PEO} = 0.3$.

The intensity ratio of the (1 2 0) peak of PEO in the mixture with the peak of pure PEO is plotted against the weight fraction in *Figure 11*. In the mixture, the intensity ratio of the sample crystallized at 500 MPa is about 17% larger than that of the sample crystallized at 0.1 MPa for $W_{PEO} = 0.9$–0.4. From these facts it is suggested that the crystallinity of PEO in the mixture crystallized under high pressure is larger than that of the sample crystallized at 0.1 MPa. If the amorphous polymer interferes with the crystallization of a crystalline polymer in the binary mixture, the lowering and broadening of the exothermic peak of crystallization occurs in thermal analysis, as reported by Nishi and Wang on the crystallization of PVDF in the mixture with PMMA[11].

In the experiment for the PCL and SAN mixture, the hindering effect of the SAN molecule on the crystallization of PCL increased with pressure, especially at low weight fraction of PCL[10]. It is considered that the opposite effect of pressure between the two mixtures on the crystallization of PEO may originate from the different interactions between the two molecular pairs. In the PEO/PMMA mixture, the interaction between the two polymer molecules is not so strong and the applied pressure may be effective in pulling apart the two different polymer molecules at the boundary during crystallization. Yamanaka *et al.*[12] carried out ^{13}C n.m.r. measurements and reported that the miscibility is strong at the chain end of PEO in the PEO/PMMA mixture. In the PCL/SAN system the interaction between the two polymers increased at elevated pressure and the crystallization of PCL was impeded by the increased entanglement.

CONCLUSIONS

The pressure change of the phase diagram of melting and crystallization of PEO in the binary mixture with PMMA was determined by high pressure d.t.a. The depression rate of T_m of PEO with decreasing PEO content did not change at elevated pressure but that of T_c decreased; it was concluded that crystallization of the PEO molecule occurs apart from the PMMA molecule under high pressure. The experimental evidence of increased intensity of the X-ray diffraction line of the sample crystallized at high pressure and the existence of a melting peak only for the sample crystallized at high pressure in $W_{PEO} = 0.3$, supports this idea. Optical microscopic observation also supports the above conclusion.

REFERENCES

1 Cortazar, M., Calahorra, E. and Guzman, G. M. *Eur. Polym. J.* 1982, **18**, 165

2 Calahorra, E., Cortazar, M. and Guzman, G. M. *Polymer* 1982, **23**, 1322

3 Calahorra, E., Cortazar, M. and Guzman, G. M. *Polymer* 1983, **24**, 211

4 Martuscelli, E., Canetti, M., Vicini, L. and Seves, A. *Polym. Commun.* 1982, **23**, 332

5 Martuscelli, E., Demma, G., Rossi, E. and Segre, A. L. *Polym. Commun.* 1983, **24**, 266

6 Addonizio, M. L., Martuscelli, E. and Silvestre, C. *Polymer* 1987, **28**, 183

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

8 Li, X. and Hsu, S. L. *J. Polym. Sci., Polym. Phys. Edn.* 1984, **22**, 1331

9 Nakafuku, C. and Yasuniwa, M. *Polym. J.* 1987, **19**, 845

10 Nakafuku, C. *Polym. J.* 1989, **21**, 781

11 Nishi, T. and Wang, T. T. *Macromolecules* 1975, **8**, 909

12 Yamanaka, A., Kaji, A. and Murano, M. *Polym. Prepr. Japan.* 1991, **40**, 1133