BLOCK COPOLYMERS POLY(2,6-DIMETHYL-1,4-PHENYLENE OXIDE)–POLY(6-HEXANELACTAM). PHYSICAL PROPERTIES

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Dedicated to Professor Otto Wichterle on the occasion of his 80th birthday.

In powdery poly(2,6-dimethyl-1,4-phenylene oxide)–poly(6-hexanelactam) diblock copolymers, the occurrence of an amorphous interphase consisting of both the blocks was indirectly proved by calorimetric and sorption methods. The copolymer shows a compatibilizing effect in solution-cast films made from the blends of both homopolymers.

Diblock copolymers poly(2,6-dimethyl-1,4-phenylene oxide) (PPO)–poly(6-hexanelactam) (PA6) were prepared by the anionic polymerization of 6-hexanelactam using PPO initiators[1]. The PPO and polyamide blocks had the number-average molecular weights $\overline{M}_n$ 6 000 – 15 000 and 30 000 – 100 000, respectively. Most of the copolymers were prepared by precipitation copolymerization in toluene in the powder form; they did not contain PPO or polyamide homopolymers.

It can be expected that these block copolymers have a three-phase structure and contain the crystalline polyamide phase and incompatible amorphous polyamide and PPO phases. Both amorphous phases are located at the surface and inside crystalline aggregates and their separation cannot be directly observed as in the copolymers with both noncrystallizing blocks[2].

This study employs methods suitable for investigating the phase properties of powdery samples in small quantities. The aim is to contribute to understanding the nature of interactions between phases of incompatible polymers chemically bonded in the diblock copolymer.

EXPERIMENTAL

Materials

The block copolymers were prepared and characterized as regards the composition in the previous paper[1]. Powdered PA6, Miramid (Leuna Werke, Germany) with $\overline{M}_n = 1.3 \cdot 10^4$ and PPO with $\overline{M}_n \approx 10^4$ (sample D in Table I, ref[1].) were used as reference materials.

Calorimetry and Thermogravimetry

All experiments were performed in a nitrogen atmosphere with the Perkin–Elmer DSC7 and TGA7 instruments interfaced with a computer data station.

For the DSC measurements, dry samples (8 – 15 mg) were heated from 30 to 250 °C at the rate 20 °C/min (first scan) and cooled to room temperature at 100 °C/min; and the second scan, cooling crystallization scan and third scan were obtained at 20 °C/min in the same temperature range. Glass transition temperatures T_g were evaluated from the second scans.

TGA was performed with 4 – 8 mg samples in the range 40 – 650 °C at the heating rate 10 °C/min. The mass loss profile is expressed in the differential form.

Water Sorption

Equilibrium sorption of water vapour was determined gravimetrically, with the polymer samples predried over P_2O_5 to a constant weight, in air of relative humidity 65% (over 36% H_2SO_4) and 93% (over saturated aqueous solution of KNO_3) at 23 °C.

Solution-Cast Films

The copolymers were dissolved in the 1 : 1 (v/v) mixture of 100% formic acid and $CHCl_3$ to approximately 5% solutions. A drop of the solution was spread on the surface of a glass slide by a glass rod and allowed to dry in air. The films of compatibilized PA6–PPO blends were prepared similarly. The film of the blend of homopolymers PA6 and PPO was prepared from a drop of the emulsion obtained by vigorous shaking equal volumes of approximately 10% solutions of PA6 in formic acid and PPO in $CHCl_3$. The micrographs were obtained with a polarizing optical microscope Photomicroscope III (Zeiss–Opton). In certain cases, the effect of the crystalline phase was diminished by setting the polarizers to off-crossed position by about 20°.

RESULTS AND DISCUSSION

Transition Phenomena

Calorimetric measurements revealed that the crystallinity of copolymer, expressed as heat of melting ΔH_m, decreases with the increasing content of PPO blocks more than it would correspond to the decrease in polyamide content. This can be seen in Fig. 1 for the first and third DSC scans. The crystallinity of original copolymers, which were separated as semicrystalline solids during precipitation copolymerization or polymerization below the melting point, is well developed and recovers from the melt only partly in the conditions of fast cooling. The excessive increase of the amorphous polyamide fraction in the first melting may indicate the formation of an amorphous interfacial volume where the PPO and polyamide blocks are chemically bound[3].

This assumption is corroborated by the increase in glass-transition temperature T_g of the polyamide phase with the increasing content of PPO blocks (Fig. 2). This shows that a part of polyamide chains directly linked to rigid PPO blocks at the interface has a lower free volume. The changes in the T_g of the PPO phase cannot be observed because the transition region overlaps with the melting peak of the crystalline polyamide (T_g of PPO initiators[1] was 208.5 – 208.8 °C).

The values of melting and crystallization temperatures corresponding respectively to the endotherm and exotherm peaks in DSC scans are more scattered when plotted vs the content of PPO blocks (Fig. 3) but show a distinct decreasing trend characteristic of crystallizing block copolymers with partial miscibility of blocks[4].

Thermal Stability

Typical differential thermogravimetric curves obtained in an inert atmosphere are shown in Fig. 4. Homopolymers corresponding to the blocks were decomposed very sharply above 400 °C (curves *1*, *2*). The block copolymers prepared by bulk copolymerization[1], which contain certain amounts of polyamide homopolymer, showed the same behaviour (curve *3*).

On the other hand, a part of the block copolymers prepared by the precipitation copolymerization in toluene decomposed at lower temperature (curve *4*). This stage of

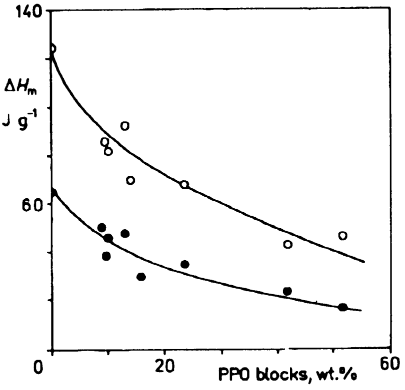


FIG. 1
The dependence of heat of melting ΔH_m of the copolymers on the PPO block content: the first (○) and second (●) DCS scan

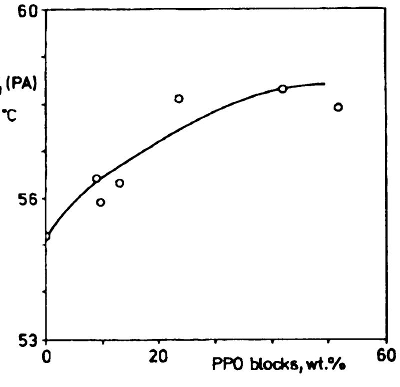


FIG. 2
The dependence of glass transition temperature T_g of the polyamide phase in the copolymers on the PPO block content

decomposition started soon after melting and was completed before the thermolytic temperature was achieved. Because the part decomposing earlier is approximately proportional to the content of polyamide segments in the copolymer, the depolymerization to the volatile 6-hexanelactam is concerned. The depolymerization is obviously induced by residues of the anionic catalytic system, i.e. by potassium amide salt units in polyamide blocks and *N*-acyllactam end groups of these blocks as the copolymers were not extracted with water. 6-Hexanelactam was detected by gas chromatography in the volatile products of decomposition carried out up to 340 °C. It was condensed in a freeze trap attached to the nitrogen outlet from TGA. After extraction with water and drying, the copolymers decomposed near 400 °C without prior depolymerization (curve *5*).

Sorption of Water Vapour

The sorption of water vapour was measured at relative air humidity 63 and 95%. The equilibrium amount of water absorbed by dry sample, w (wt.%), was recalculated to the amorphous fraction of polyamide:

$$w_a = w/[w_{PA} - (\Delta H_m/\Delta H_m^0)]\,,$$

where w_a (wt.%) is water absorbed in the amorphous polyamide, w_{PA} is the weight fraction of polyamide in copolymer, ΔH_m (J g^{-1}) is the heat of melting determined in

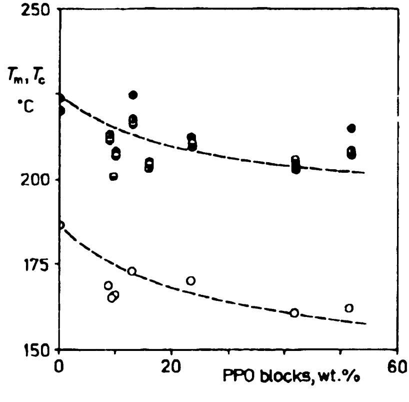


FIG. 3
The dependence of melting (●, ◑, ◒) and crystallization temperatures (○) of the copolymers on the PPO block content: the first (●), second (◑) and third (◒) DSC scan

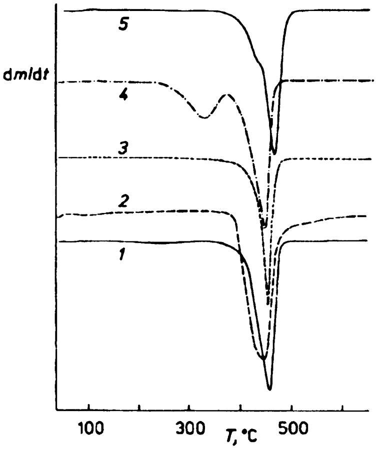


FIG. 4
Thermogravimetric curves of PA6 (*1*) and PPO (*2*) homopolymers and diblock copolymers prepared by bulk (*3*) and precipitation copolymerization before (*4*) and after (*5*) extraction with water

the first DSC scan and ΔH^0_m = 230 J g^{-1} is heat of melting of the crystalline α-modification of PA6 (ref.[5]). The w_a values plotted in Fig. 5 show a striking decrease with the increasing content of PPO blocks. This is obviously caused by the fact that a part of amorphous polyamide is affected by binding to PPO blocks and the sorption of water into this interfacial volume is hindered by the decreased free volume.

Morphology of Solution-Cast Films

The block copolymers are insoluble in typical solvents of PA6, such as *m*-cresol, fluoroalcohols and formic acid and also in typical solvents of PPO (aromatic hydrocarbons, chloroalkanes). They dissolve in the 1 : 1 (v/v) mixture of chloroform and 100% formic acid to more or less opalescent solutions. The copolymers containing more than 40% PPO blocks require a higher proportion of $CHCl_3$ in the mixed solvent for dissolution.

The solutions containing about 5 wt.% of copolymers gave, by free evaporation on a glass slide, thin films with a uniform crystalline structure visible in an optical microscope between crossed polarizers (Fig. 6*a*). The crystallites in the copolymers containing more than 40 wt.% PPO blocks become very fine and hardly observable.

In a similar way, the compatibilization effect of the block copolymer was tested in the solution-cast films of PA6–PPO blends. The micrographs in Figs 6*b* and 6*c* belong to the films cast from a 1 : 1 (w/w) mixture of homopolymers obtained by mixing of separately prepared solutions in formic acid and $CHCl_3$, respectively. The resulting emulsion gave the film with roughly separated phases where polyamide forms large crystallites (Fig. 6*b*) and PPO is concentrated in dark drops of various size visible between off-crossed polarizers (Fig. 6*c*). On the other hand, the ternary 1 : 1 : 1 (w/w/w) mixture of polyamide, PPO and the block copolymer containing 9 wt.% PPO blocks formed a typical opalescent solution and the film with crystalline structure very similar to that of the neat copolymer (Fig. 6*d*). The decreasing content of the compati-

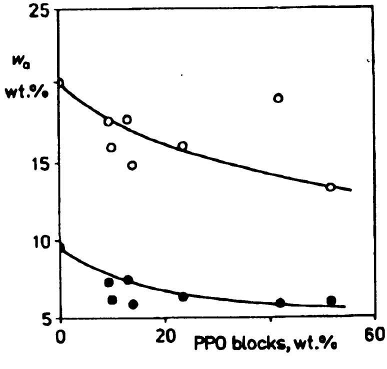
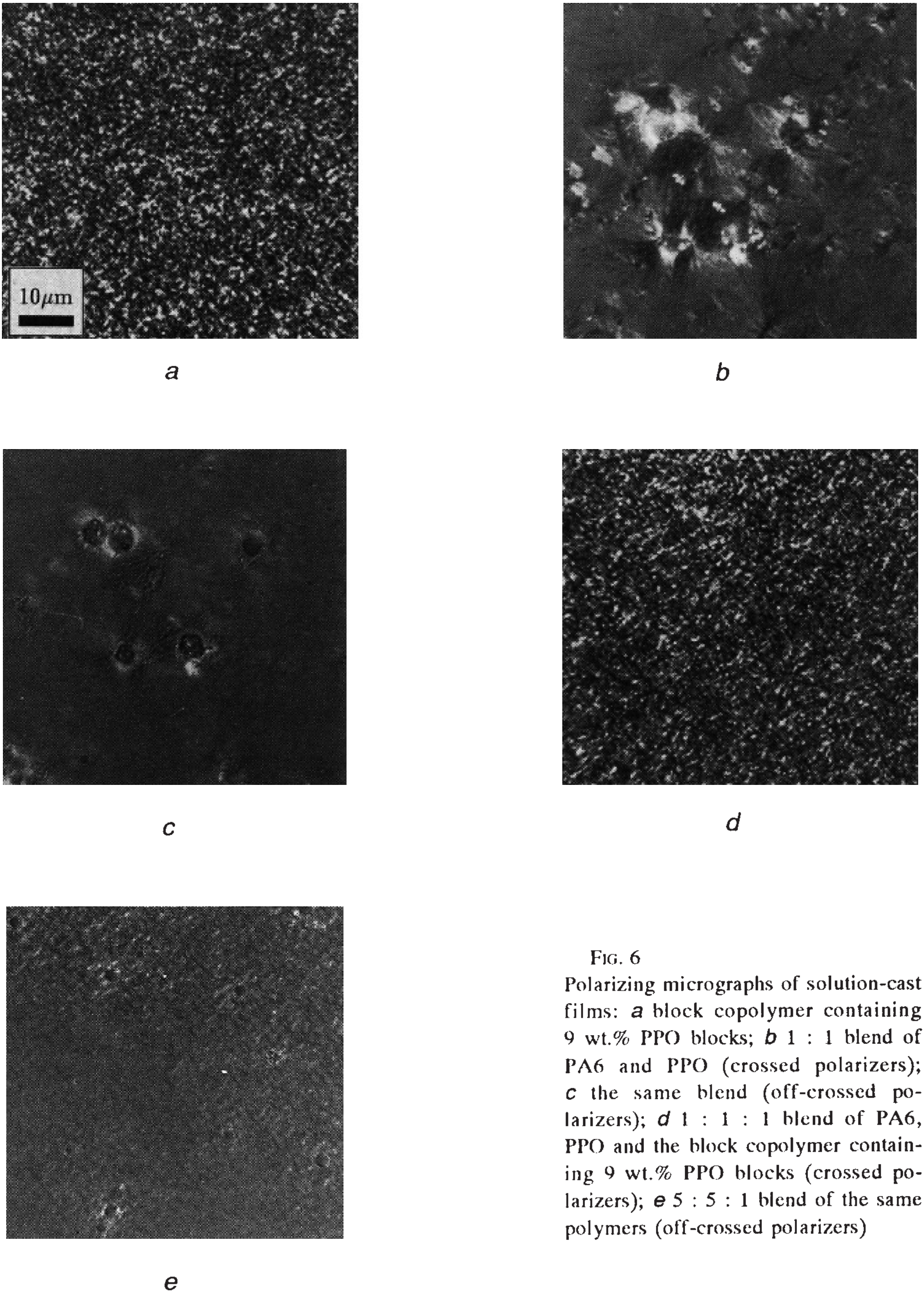


FIG. 5

The dependence of equilibrium water content in the block copolymers (related to the fraction of amorphous polyamide) at 23 °C and relative humidity 93% (○) and 65% (●) on the PPO block content



a *b* *c* *d* *e*

FIG. 6
Polarizing micrographs of solution-cast films: *a* block copolymer containing 9 wt.% PPO blocks; *b* 1 : 1 blend of PA6 and PPO (crossed polarizers); *c* the same blend (off-crossed polarizers); *d* 1 : 1 : 1 blend of PA6, PPO and the block copolymer containing 9 wt.% PPO blocks (crossed polarizers); *e* 5 : 5 : 1 blend of the same polymers (off-crossed polarizers)

bilizer led to the solution-cast films with the increasing size of polyamide crystallites and to the occurrence of isolated drops of PPO (Fig. 6*e*), about one tenth in size when compared with those in polymer blends prepared from the melt[6].

CONCLUSION

An excessive decrease in the heat of melting, increasing T_g of the polyamide phase and a decreasing trend of melting temperature of crystalline polyamide accompanying the increase in PPO proportion are an indirect evidence for the existence of an interphase combining the segments of incompatible polymer blocks. In spite of the amorphous polyamide fraction increasing with the increasing content of PPO blocks in the copolymer, an unexpected decrease in the water sorption by polyamide occurs. This is a more distinct proof of the occurrence of an amorphous interfacial volume with the hindered access of water caused by the presence of PPO blocks.

The compatibilizing effect of the poly(2,6-dimethyl-1,4-phenylene oxide)–poly(6-hexanelactam) block copolymer in the blends of PPO and PA6 was confirmed by the morphology of solution-cast films.

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