Compatibilizing Effect of a Diblock Copolymer of Isotactic Polystyrene and Isotactic Polypropylene in Blends of the Corresponding Homopolymers*

L. DEL GIUDICE, R. E. COHEN,[†] G. ATTALLA, and F. BERTINOTTI,
*Istituto G. Donegani S.p.A., Novara Research Center, Montedison Group,
Via Fauser 4, 28100 Novara, Italy*

Synopsis

A high molecular weight polymer mixture was obtained from a sequential Ziegler–Natta polymerization of styrene and propylene. After removing unwanted homopolymers from the reaction product, the remaining copolymer was subjected to extensive molecular and morphological characterization. The results of these experiments indicate that the purified material is a diblock copolymer of isotactic polystyrene and isotactic polypropylene, with each block having a molecular weight in the range of 225,000 g/mol. This block copolymer was incorporated in varying amounts into blends of isotactic polystyrene and isotactic polypropylene homopolymers. At low concentrations of copolymer (<20 wt %), the diblock functions as a dispersing agent, significantly reducing the size of domains in the heterogeneous blends. At higher copolymer concentrations, a dramatic improvement in the adhesion across the domain boundaries is also observed. The favorable effects of the copolymer on mechanical properties are demonstrated in the results of tensile impact experiments.

INTRODUCTION

In spite of the large quantity of research on copolymer blends carried out during the past 10 years, intense activity in this field continues unabated at the present time.[1-4] This is largely due to the need for providing materials with specified properties for various applications without resorting to the production of previously unknown polymer. It has been found in many cases that blends of readily available polymers can indeed meet performance specifications, particularly when a polymeric "compatibilizing agent" is employed in the blending process. These compatibilizers generally have a twofold function: to reduce the characteristic domain size of the heterogeneous morphology of the blend and to enhance adhesion by providing a certain amount of chemical bonding across domain boundaries.

Much of the work in this field has been conducted on blends comprised of pairs of amorphous thermoplastic polymers.[1] One of the reasons for this emphasis is the relative ease with which the compatibilizers (usually block or graft copolymers) can be synthesized for use in the amorphous/amorphous system. A certain amount of literature also exists for the case of polymer pairs in which one component is semicrystalline and the other amorphous.[1] However, except for the particular case in which both polymers are olefin-based,[1] essentially nothing has been reported on compatibilized

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* This paper is dedicated to the memory of Prof. Floriana Bertinotti.

[†] Permanent address: Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139.

blends of two semicrystalline polymers; here the problem of synthesizing a semicrystalline/semicrystalline block or graft copolymer to serve as the compatibilizer has probably played a large role in retarding research.

In the present paper we report on our recent work in this largely unexplored area of compatibilized semicrystalline polymer blends. Our work has focused on the system comprised of homopolymers of isotactic polystyrene and isotactic polypropylene and a corresponding diblock copolymer.

EXPERIMENTAL

The materials used in this study were: a commercial isotactic polypropylene (iPP) (Moplen MO/S, $\overline{M}_w = 450,000$ g/mol), an isotactic polystyrene (iPS) ($\overline{M}_w = 500,000$ g/mol) polymerized in a laboratory-scale reactor using a Ziegler–Natta catalyst and a copolymer obtained by sequential polymerization of styrene and propylene using a Ziegler–Natta catalyst (COP iPS–iPP).[5]

The copolymer was separated from unwanted homopolymer species in the product mixture obtained from the sequential copolymerization using the following procedure. A 5% solution of the product (with heat stabilizers added) in α-chloronaphthylene was heated to 160°C in a jacketed separatory funnel. The clear solution was cooled at a rate of 0.5°C/min; at 95°C the first crystals appeared. The temperature was maintained at 95°C for several hours to allow this fraction to crystallize from solution. Experiments on the two homopolymers showed that, using the same procedures, isotactic polypropylene crystallizes at 110°C and isotactic polystyrene does not crystallize. Thus the fraction isolated at 95°C was felt to be comprised essentially of copolymer species, with the possibility of some low molecular weight polypropylene species also being present. To remove the latter, the crystallized fraction was redissolved in orthodichlorobenzene, filtered, precipitated in methanol, and finally extracted with boiling heptane for 12 h. After all of the purification steps, the residual copolymer fraction represented only 20% by weight of the original reaction product. This purified copolymer was subjected to extensive characterization as described in the next section.

Blends of iPS, iPP, and COP iPS–iPP were prepared by dissolving the polymers and an antioxidant (Irganox 1076) in orthodichlorobenzene at 160°C and precipitating the polymers using a 1:1 mixture of acetone and methanol. The precipitated powders were dried and compression-molded into sheets suitable for cutting specimens for mechanical testing. Tensile impact resistance was determined for various blends and for the pure components using an instrumented pendulum. ASTM procedure D1822 with sample type S was employed.

RESULTS AND DISCUSSION

Characterization of Copolymer Molecular Structure and Morphology

Prior to exploring its potential as a compatibilizing agent for isotactic polystyrene/isotactic polypropylene blends, extensive molecular and morphological characterization was carried out on the purified copolymer. In

particular, we felt that it was essential to establish unequivocally the block-like nature of the copolymer since, to our knowledge, there have been no prior reports of this molecular structure in the literature for the particular case of iPS and iPP.

The chemical composition of the copolymer was determined by infrared analysis and by combustion elemental analysis. The IR experiments yielded compositions of 48 and 57 wt % polystyrene in duplicate tests; the elemental analysis showed 89.34 wt % carbon and 10.60 wt % hydrogen, which translates to a copolymer composition of about 55 wt % polystyrene. Based on these results, we considered the copolymer to be comprised of essentially 50 wt % of each component. The overall molecular weight of the copolymer was difficult to determine with precision owing to its limited solubility; nevertheless, based on high temperature dilute solution viscosity measurements and high temperature GPC experiments, we estimate the copolymer molecular weight to be in the range of 330,000–570,000 g/mol.

Differential scanning calorimetry on the copolymer revealed two strong first order transitions (Fig. 1) at 161 and 227°C, respectively, suggesting a considerable amount of polypropylene and polystyrene crystallinity. The melting points of the two homopolymers determined under similar conditions are 167 and 225°C. Wide angle X-ray scattering revealed significant overall crystallinity in the copolymer, but it was not possible to make a quantitative determination of the crystalline content of each component owing to the overlap of the various peaks in the X-ray spectrum.

High resolution C^{13}-NMR experiments provided the first important clues regarding the molecular architecture of the copolymer. In the spectrum shown in Figure 2, all of the clearly identifiable peaks (i.e., those not masked by the solvent) are located in the exact positions exhibited by the respective homopolymers. There are no measurable shifts of peak locations which might be interpreted in terms of propylene–styrene repeat unit interactions. This information leads to the conclusion that the purified product of the sequential copolymerization is either a block copolymer with two (or perhaps a few) long sequences of essentially pure isotactic polystyrene and isotactic polypropylene, or a simple mixture of the two homopolymers. In order to eliminate the latter possibility and to substantiate the former, the following experimental results were obtained.
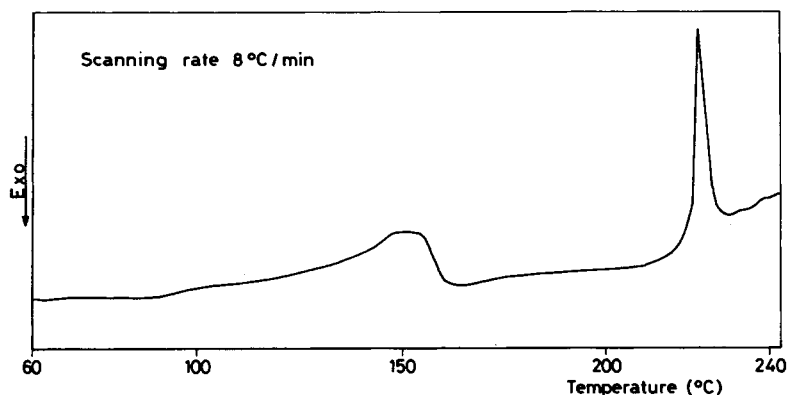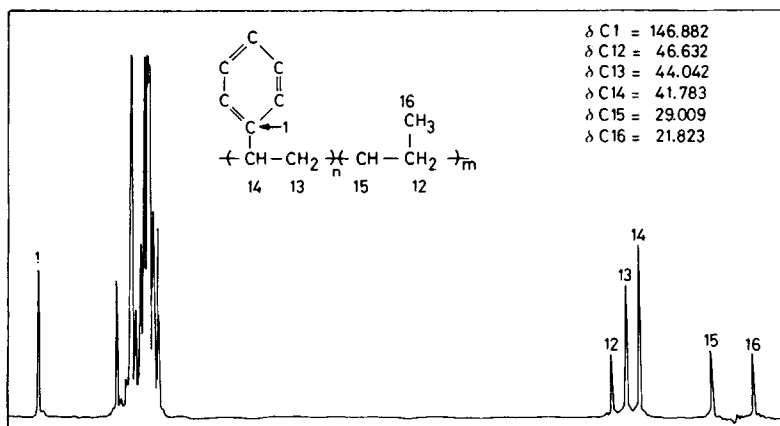

Fig. 1. DSC thermogram of COP iPS–iPP.

Fig. 2.   C[13]-NMR spectrum of COP iPS–iPP.

In Figure 3 two photographs are shown, both obtained under identical conditions in a polarizing light microscope. The homopolymer blend (50 wt % of each component) exhibits, as expected, a morphology consisting of large, irregular regions (> 10 μm) of each phase. The copolymer has a much different morphology, showing only a finely dispersed submicron structure throughout the field of view. Verification of this apparent microphase separation was sought using transmission electron microscopy. Unfortunately, the isotactic polystyrene and isotactic polypropylene constituents of the blends and the diblock copolymer studied here do not lend themselves readily to selective staining procedures often employed for polystyrene/polydiene systems. Nevertheless, we attempted to enhance contrast through the use of osmium tetroxide hoping that the low *Tg* amorphous regions of iPP might acquire a higher-than-average concentration of osmium metal, thereby improving the quality of micrographs. Results of these experiments can be summarized as follows: Unstained block copolymer and blends revealed essentially no structure in the TEM. Stained samples revealed readily visible contrast; the characteristic phase size in the blend was greater than 10μm, with no small-scale structure visible at higher magnifications. The diblock showed structural features ranging from several microns to hundreds of Angström units. This result is shown in Figure 4 where the dark regions are presumed to be the osmium-rich polypropylene phases. The presence of structural features at the level of 1000 Å and smaller is consistent with the suggested diblock structure for the copolymer. The larger dark regions may reflect the presence of unwanted polypropylene homopolymer remaining after the purification process. As a final note in regard to the transmission electron microscopy studies, it was exceedingly difficult to obtain ultramicrotomed sections of the blend whereas the diblock copolymer could be cut with relative ease. This points out yet another of the major differences between the copolymer and the corresponding homopolymer blend.

A final set of comparative microscopy experiments was carried out on a scanning electron microscope. Prior to gold decoration, a copolymer specimen and a 50/50 homopolymer blend were cut with a glass knife and the
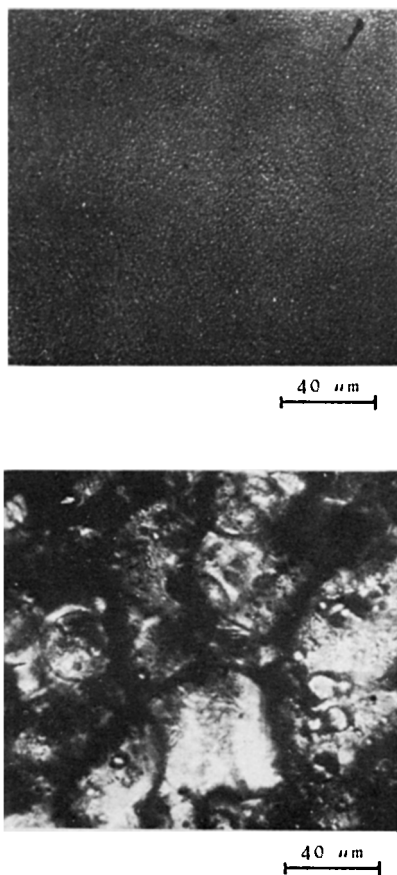
40 μm

40 μm

Fig. 3. Polarized light micrographs of COP iPS–iPP (top) and 50/50 iPS/iPP blend.

surfaces were exposed to vapors of allylamine at room temperature for 1 h. Figure 5 again reveals a clear difference between the blend and the copolymer; the macrophase separation clearly revealed on the etched surface of the blend is not present in the copolymer

Significant differences in dynamic mechanical behavior are also seen when the copolymer and the homopolymer blend are compared. Figure 6 shows the results of free-oscillation torsion pendulum experiments for these two materials. The blend shows two distinct transitions at 0 and 90°C which result from the glass transitions of the two phases. Evidence that the phases are wedded together to a greater extent in the copolymer may be inferred from the more gradual drop in modulus shown by this sample in Figure 6.

Taken all together, the comparative information obtained from the various microscopy and dynamic mechanical experiments described immediately above indicates that the purified product of the copolymerization reaction is definitely not a simple blend of homopolymers. Furthermore, the fact that the copolymer is comprised of strongly connected, submicron-sized phases supports a molecular architecture of the block copolymer type. Thus, from all the facts presented in this section, coupled with the synthesis
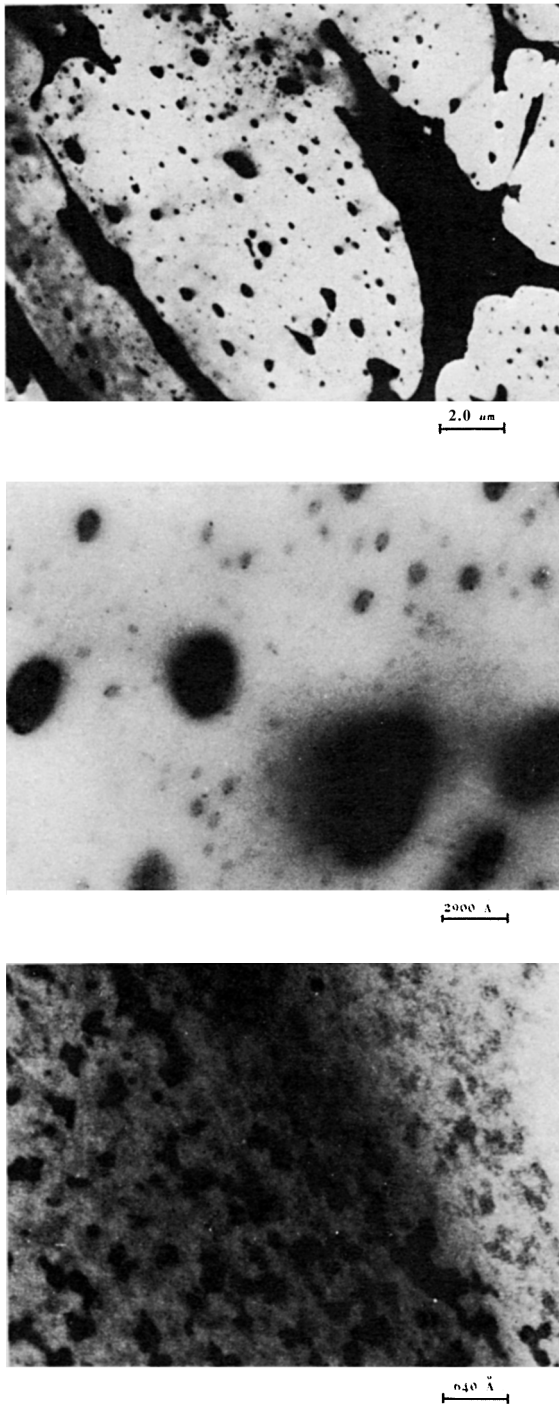
Fig. 4.   TEM micrographs of COP iPS–iPP at different magnifications.
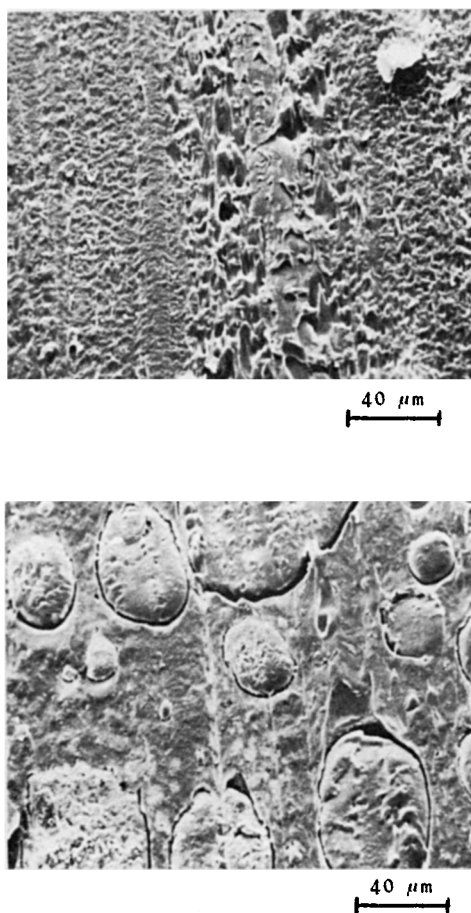
Fig. 5. SEM micrographs of COP iPS–iPP (top) and 50/50 iPS/iPP blend after etching with allylamine vapors.

methods used, we conclude that the purified reaction product is a diblock copolymer consisting of linear chain molecules, each of which contains a single long sequence of isotactic polystyrene ($\overline{M}_w \sim 225{,}000$), which is covalently linked to a single long sequence of isotactic polypropylene of about the same molecular weight.

Effect of Block Copolymer on iPS/iPP Blends

Following the characterization of COP iPS–iPP, we focused our attention on its influence on the structure and properties of various blends of iPS and iPP. In particular, we wished to determine whether or not the block copolymer could function as a "compatibilizing agent" in these blends. More specifically, we examined the possibility of a systematic reduction in particle size in these heterogeneous blends as copolymer content was increased and the further possibility that the copolymer might promote adhesion between the phases. Finally we sought to establish connections between observed morphological changes and mechanical properties. Figure 7 provides a schematic representation of the scope of the work on blends of iPS and iPP and
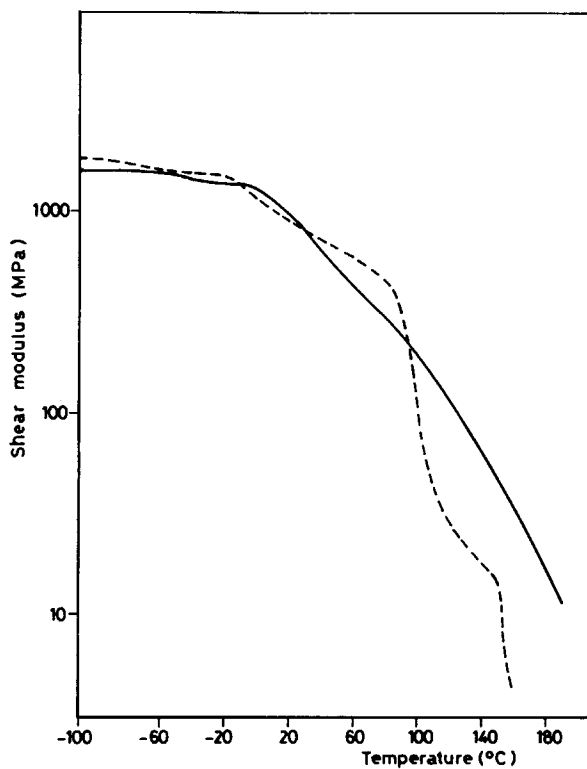
Fig. 6. Dynamic mechanical spectrum of COP iPS–iPP and 50/50 iPS–iPP blend obtained with a free-oscillation torsion pendulum: (—) COP iPS–iPP; (- - -) 50/50 iPS/iPP blend.
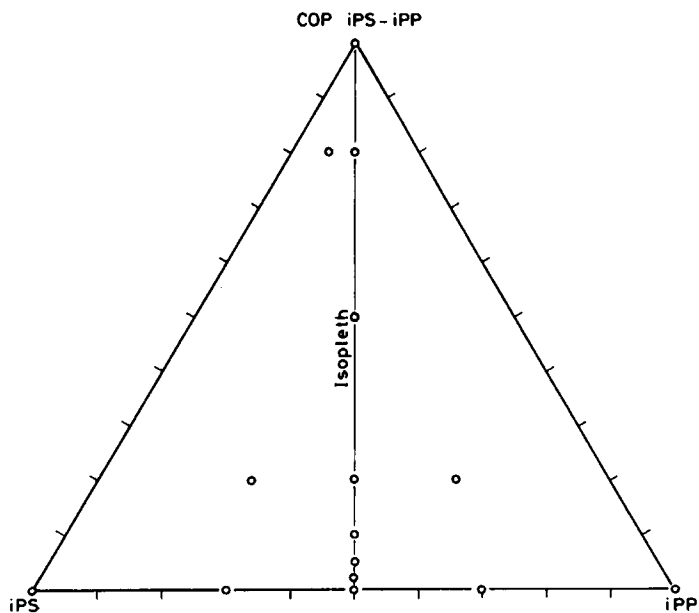

Fig. 7. Triangular phase diagram showing the compositions examined.

block copolymer. In addition to the three pure components shown at the vertices of the triangular diagram, we examined three binary blends of iPS and iPP, represented by the points along the base of the triangle, and nine ternary blends, represented by points in the interior of the triangle. Because the copolymer is itself a material of about 50 wt % polystyrene and 50 wt % polypropylene, the isopleth or line of constant composition is a straight line connecting the copolymer vertex with the center of the base of the triangle. Along the isopleth, all materials contain equal weight percentages of propylene and styrene repeat units while the copolymer content varies from 100 to 0% as one travels from vertex to base.

Figure 8 provides the first indication of the "morphology-regulating" capacity of COP iPS–iPP. In this figure, polarized light micrographs are shown for various ternary blends taken along the isopleth. It is clear that increased amounts of copolymer result in morphologies of finer scales. Taken together, Figures 3 and 8 indicate that upon addition of as little as 5 wt % diblock copolymer, the coarse morphology of the homopolymer blend is dramatically changed, and that this is followed by a smooth and continuous reduction in grain size as the concentration of diblock copolymer approaches unity.

The series of scanning electron micrographs shown in Figure 9 supports the above findings. The observed surface morphologies, obtained by fracturing specimens in liquid nitrogen, reveal a clear trend; a pattern of ever-smaller scale is observed as copolymer content increases. In three of the materials (0,2, and 5% copolymer) there is clear evidence of slippage between the two dissimilar components. Smooth surfaces are seen on the large protrusions and craters formed during the fracture process, indicating little or no adhesion between iPS and iPP. At higher concentrations of diblock (20, 80, and 100%) a different behavior is observed. The surfaces of these three materials reveal a level of roughness which is not seen at lower copolymer contents.

At higher magnification (Fig. 10) it is apparent that part of the source of this roughness is the presence of stretched and broken fibrils of material, which in the blends containing 20 and 80% copolymer appear to span the interfaces between regions of iPP and iPS. This enhanced adhesion is particularly evident in the micrograph for the blend containing 80% copolymer in Figure 10. Also, for this blend there are numerous examples of dispersed particles which have been broken in the plane of fracture, with essentially no slippage occurring. Similar observations have been made by Heikens and co-workers[6] for blends of atactic polystyrene, low-density polyethylene, and the corresponding graft or block copolymer. Thus, at high concentrations the block copolymer appears to function both as a dispersant, reducing the characteristic size of the heterogeneous morphology, and as a coupling agent, providing significantly improved adhesion between the continuous and dispersed zones in the blend.

The effect of these two functions of the diblock copolymer on mechanical properties was examined in the tensile impact experiments described in the Experimental section. Figure 11 shows typical results obtained directly from the instrumented impact tester. From these force–time curves we obtained two quantities: E, the energy required to fracture the sample, and σ_B, the
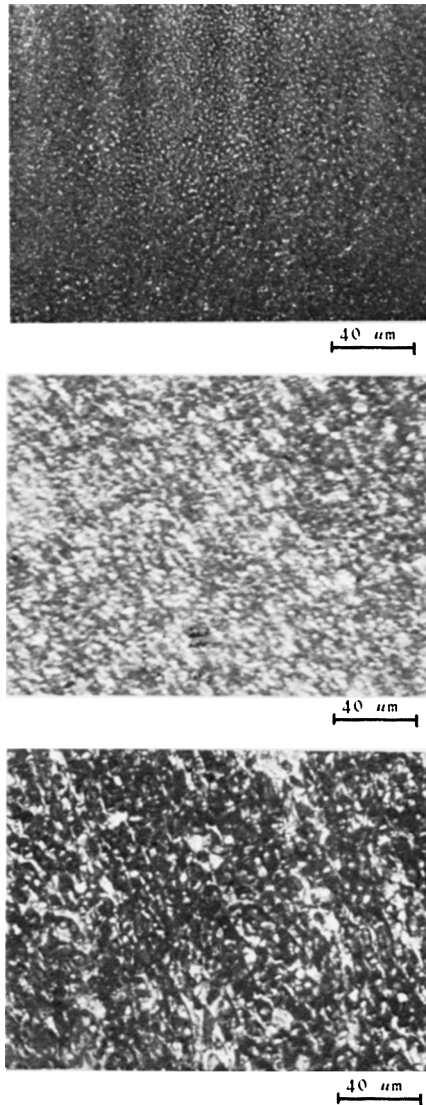
Fig. 8.   Polarized light micrographs of 50/50 iPS/iPP blends containing different amounts of COP iPS–iPP (top to bottom: 80, 20, and 5%).

stress at break, taken as the peak stress in these experiments. Figure 12 shows a plot of the breaking energy as a function of copolymer content for various blends taken along the isopleth. In addition to noting the clear trend of increased impact resistance with increased copolymer content, we also note that a typical high impact polystyrene yields a value of $E = 22$ kJ/m^2. At 20% copolymer content the iPS/iPP blends along the isopleth already exceed this value, and at very high copolymer contents the breaking energy is more than double that of a typical HIPS. Also of interest is the fact that a polystyrene-rich composition (66 wt %) containing 20% copoly-
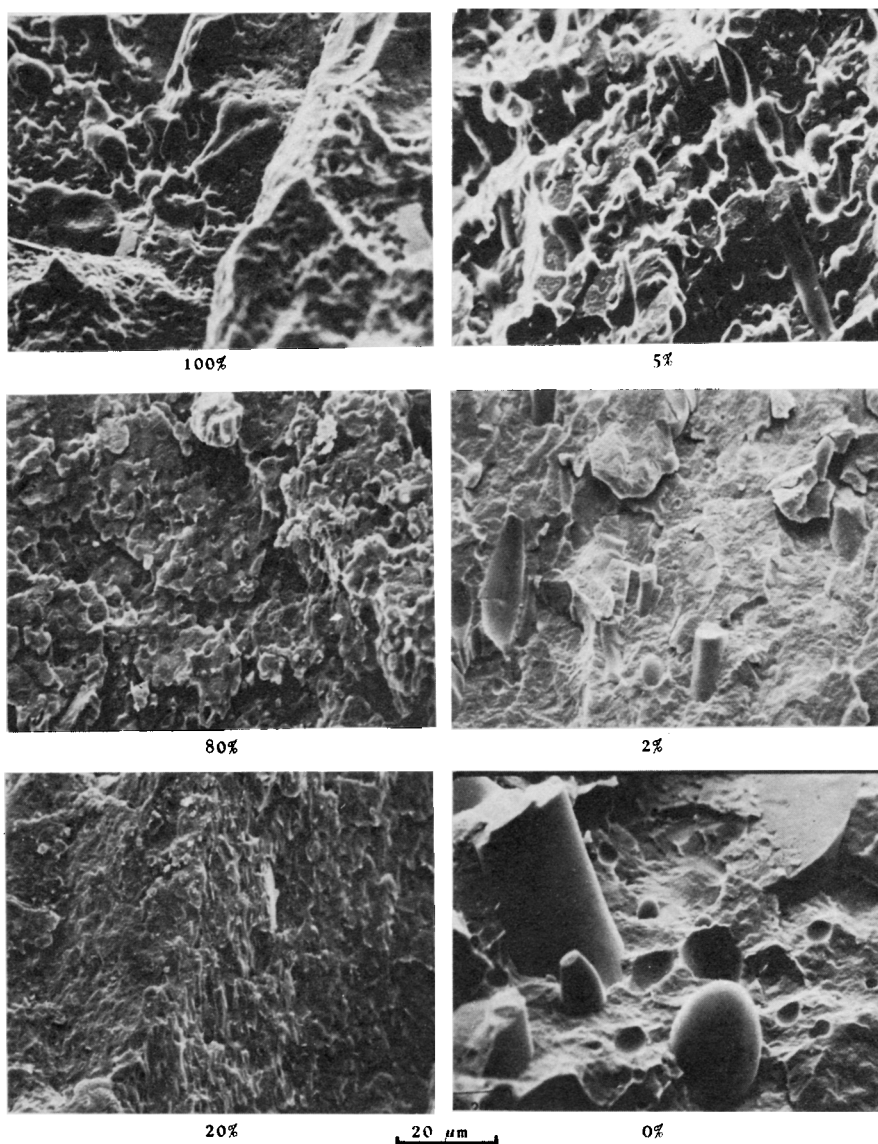
Fig. 9. SEM micrographs of 50/50 iPS/iPP blends containing different amounts of COP iPS–iPP, fractured at light nitrogen temperature.

mer also exhibited values of E well above that of HIPS. A final point regarding the synergistic effect of the copolymer in these blends is the fact that in essentially all cases in which the copolymer content was 5% or greater, the observed breaking energies were greater than the appropriate weighted-average value obtained from data on the iPS and iPP homopolymers. Identical statements can be made regarding the stress at break since in our experiments this parameter varies essentially in direct proportion to the breaking energy.
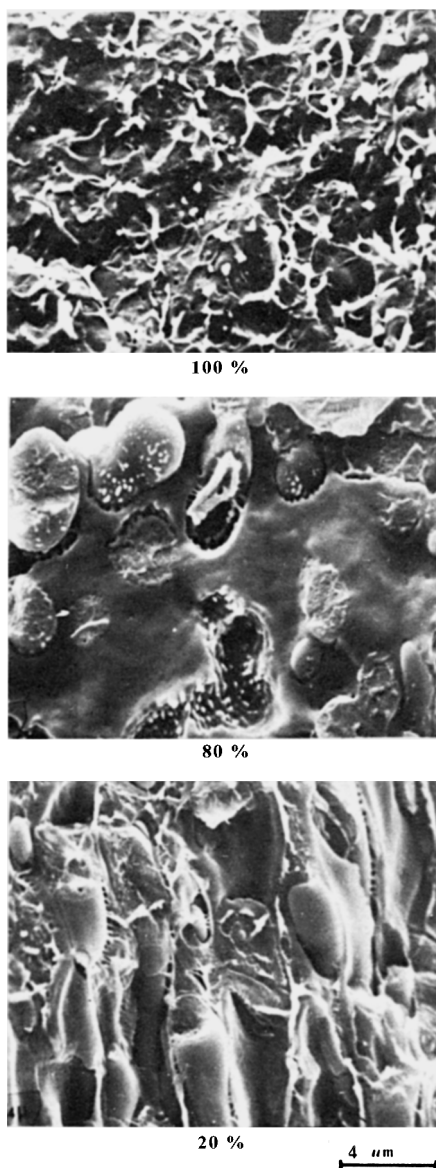
100 %

80 %

20 %   4 μm

Fig. 10. SEM micrographs of three of the blends shown in Figure 10, at higher magnification.

CONCLUSIONS

The results presented in this paper are twofold in nature. The first aspect is concerned with the possibility of obtaining a new copolymer with interesting properties from a sequential copolymerization of styrene and propylene using Ziegler–Natta catalyst. The second is related to the compatibilizing effect of this copolymer in blends of isotactic polystyrene and isotactic polypropylene.

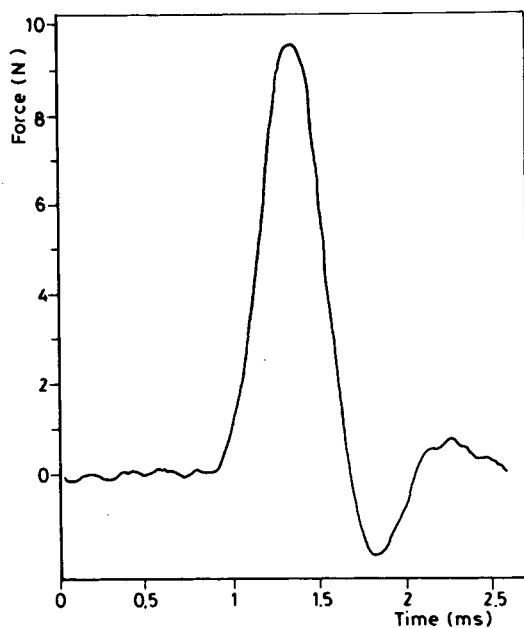Regarding the first point, the extremely fine morphology exhibited by

Fig. 11.   Typical force vs. time curve obtained from the instrumented impact tester (blend 80/10/10 COP iPS–iPP/iPS/iPP).

the copolymer (Fig. 4) is partially responsible for its unusual properties; in addition, as a consequence of the blocklike molecular architecture, the interfaces between the phases in this material are well-bonded. Comparing the shear modulus vs. temperature curves of the copolymer and the corresponding blend (Fig. 6) reveals how significant these two factors are on the mechanical behavior in the intertransitional zone and above the polystyrene glass transition. As far as impact behavior is concerned, the co-
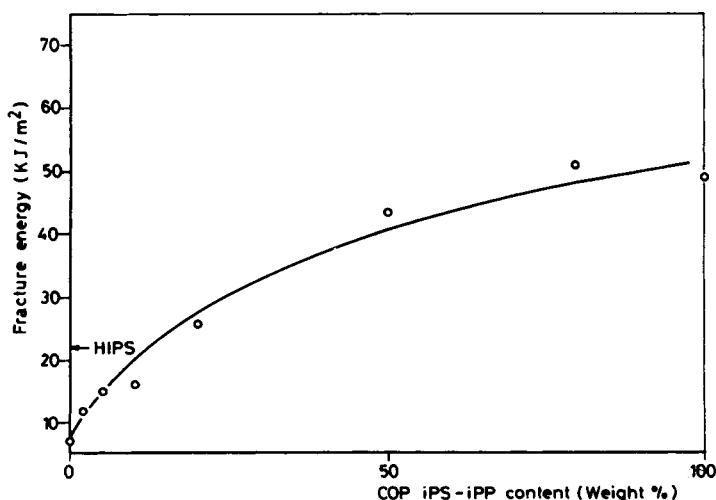

Fig. 12.   Fracture energy vs. copolymer content of COP iPS–iPP/iPS/iPP blends along the isopleth.

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polymer has an impact resistance double that of polypropylene, five times that of polystyrene, and about eight times that of the corresponding homopolymer blend. This indicates that when iPS and iPP are blended very intimately, as in the case of the diblock copolymer, it is possible to achieve impact resistances far above the level expected from a linear combination of the impact resistances of the two homopolymers.

Regarding the second point, we have demonstrated that the addition of the diblock copolymer to blends of iPS and iPP influences dramatically the phase distribution, even if the amount added is as small as 5%; the higher the copolymer content, the finer the morphology of the blend. When 20 % or more of the copolymer is added to 50/50 blends of iPS and iPP, adhesion between these two incompatible polymers is promoted and mechanically induced slippage between the iPS and iPP phases is retarded. These more intimately blended materials exhibit enhanced impact strengths, also well above the levels predicted by linear combinations of homopolymer data. Conversely, impact strengths of blends without copolymer are lower than predicted by the same linear relationship.

To conclude, we believe that future work should be carried out in two directions. Other diblock copolymers should be prepared, ideally with greater yields, containing various combinations of composition and molecular weight. This would enable work to be carried out along various isopleths using triangular diagrams such as that of Figure 8 for guidance. In addition, different blending methods, perhaps more suited to industrial application, should be explored as alternatives to the precipitation technique used in this work.

References

1. J. A. Manson and L. H. Sperling, *Polymer Blends and Composites*, Plenum, New York, 1976.

2. D. Klempner and K. C. Frisch, Eds., *Polymer Alloys*, Plenum, New York, 1977.

3. D. R. Paul and S. Newman, Eds., *Polymer Blends*, Academic, New York, 1978.

4. O. Olabisi, L. M. Robeson, and M. T. Shaw, *Polymer–Polymer Miscibility*, Academic, New York, 1979.

5. Itn Pat. Appl. 22386 A/82 (1982); Eur. Pat. Appl. 99,271 (1984).

6. S. D. Sjoerdsma, A. C. A. M. Bleijenberg, R. Palumbo, and M. Kryszewski, Eds., and D. Heikens, in *Polymer Blends; Processing, Morphology and Properties*, E. Martuscelli, Plenum, New York, 1980, p. 201.