Influence of additives on the structure and properties of polymers: 2. Polymorphic transitions of isotactic polypropylene caused by aminosulphur compounds*

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INTRODUCTION

Although the structures of the α, β, γ crystalline forms of isotactic polypropylene (iPP) are well known, there still remains the problem of agents causing the formation and transition of these forms.

The monoclinic α-form of iPP, arising during a slow crystallization, was determined by Natta and Corradini in 1960[1], whereas the existence of the hexagonal β-form was reported for the first time by Keith and Padden[2] and also by Turner-Jones[3]. Apart from these α and β forms the literature notes a triclinic γ-form[4] arising under special thermodynamic conditions.

According to Turner-Jones, the essential factor which causes structural $\alpha \rightarrow \beta$ transitions is the thermal energy[3]. Mostly the β-form (hex PP) arises when molten samples are cooled rapidly from 180° to 130°C. Dragan *et al.*[5] found that the hex PP is produced during shear-induced crystallization, whereas Leugering mentions that the β-form together with the α-form arises during crystallization of the molten iPP, containing the dye Permanent Red E3B[6].

The influence of a small amount of additives (stabilizers) on the formation and stability of crystalline structures (particularly of polyamide) was reported by us previously[7,8].

In this paper we examine the relationship between the molecular and crystal structure of stabilizers and isotactic polypropylene during crystallization from a melt. The stabilizers we used were aromatic amines and their sulphur analogues. This choice was dictated by the fact that amine-sulphur compounds prove to be better stabilizers, and their molecules are more rigid than their amine-analogues.

EXPERIMENTAL

In our investigations we have used isotactic polypropylene (iPP) without stabilizers (Petrochemistry-Plock Poland) having melting point 176°C. Chemically pure benzimidazole (BIM), 2-mercaptobenzimidazole (MBIM), diphenylamine (DFA), phenothiazine (PT), *N,N'*-diphenyl-*p*-phenylenediamine (DPFA) and triphenodithiazine (TPDT) were used as stabilizers. Descriptions of these compounds are given in *Table 1*.

These stabilizers in amounts of 0.5% in acetone solution were mixed with powdered iPP and the solvent was evaporated under reduced pressure at 30°C with continuous stirring. As TPDT is insoluble in acetone, it was mixed with polypropylene mechanically.

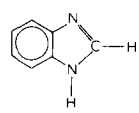
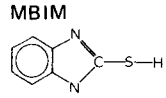
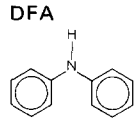
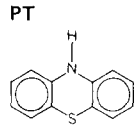
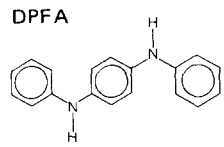
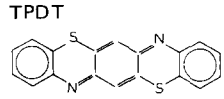
The samples were melted in a nitrogen atmosphere on a microscope hot stage, kept at 210°C for 15 min and subsequently cooled slowly. Observations of the sample in polarised light showed homogeniety of the melts.

Structural investigations were carried out by means of X-ray diffraction, measurements being made on a semi-automatic horizontal diffractometer TUR-M62, using Cu Kα radiation.

RESULTS AND DISCUSSION

The structure investigation showed the X-ray diffraction pattern of the polypropylene samples containing PT, MBIM and TPDT to be different from the others, with an additional peak at $\theta = 8.1°$, and wellmarked widening and increase of the maximum at $\theta = 10.6°$ (*Figure 1*).

Table 1 Characteristics of the compounds introduced to iPP

Compounds	M.pt. (°C)	Shape	Space group	Ref.
BIM 	170	plates	$P2_1nb$	(9)
MBIM 	281	needles	$P2_1/m$	(10)
DFA 	53	leaflets	$P\bar{1}$	(11)
PT 	180	leaflets	Pnma	(12)
DPFA 	145	plates	Pbca	(13)
TPDT 	321	needles	$P2_1/c$	(14)

* A preliminary report of this work has been presented at 5 th European Crystallographic Meeting, Copenhagen Denmark 13-17 August 1979

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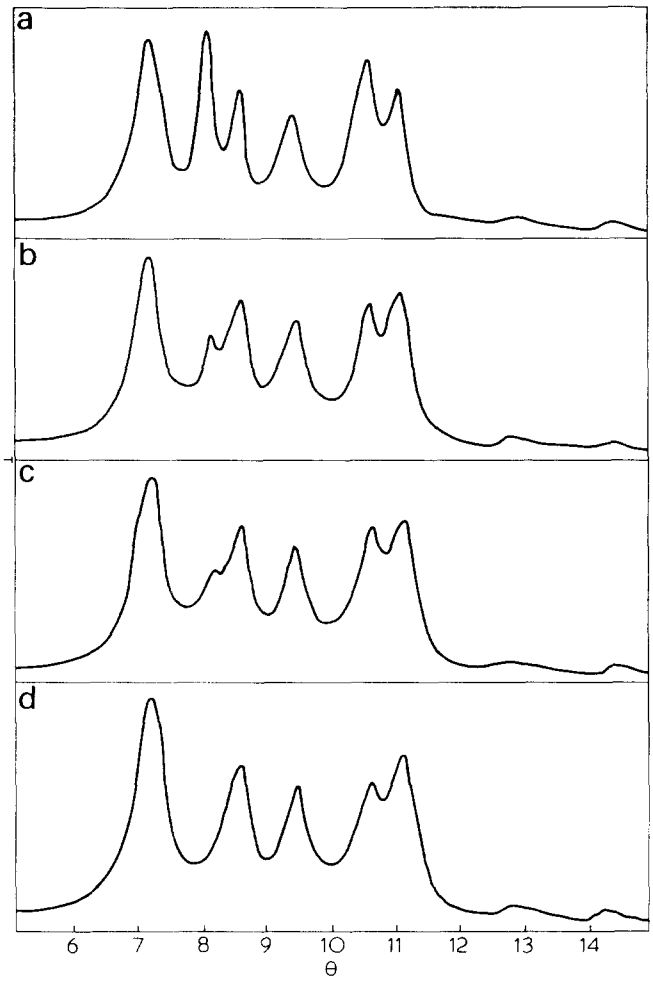


Figure 1 X-ray diffraction pattern of samples of iPP containing various additives (a) iPP with BTPT; (b) iPP with PT; (c) iPP with MBIM; (d) iPP without additives and iPP with BIM, iPP with DAF, iPP with DPFA

According to Turner-Jones[3], these two peaks indicate without doubt presence of the hexagonal β-form of the isotactic polypropylene.

The amounts of β-form in iPP (k) were determined by using the Turner-Jones equation:

$$k = \frac{I_{\beta_1}}{I_{\beta_1} + (I_{\alpha_1} + I_{\alpha_2} + I_{\alpha_3})}$$

where k = amount of the β-form, I_{β_1} = height of the peak from the β-phase (at $\theta = 8.1°$), I_{α_1} = height of the peak from the α-phase (at $\theta = 7.1°$, $\theta = 8.5°$, $\theta = 9.4°$).

The thermal ageing was achieved at 120°C for 6 h in a dryer with circulating air.

Analysis of the height of the peaks according to the above equation indicated the maximum contribution (28%) of the hexagonal phase in samples containing TPDT (*Table 2*).

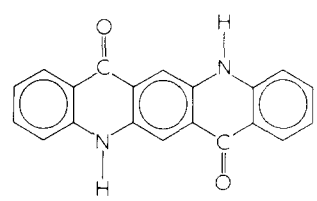
The values given in *Table 2* show that the β-form arises in the presence of the stabilizers having melting points higher than that of iPP. This suggests the heterogeneous nucleation, while lowering the temperature of the melt, first crystallizes the stabilizer and the crystals act as nucleating agents.

There is no close relation between the melting point of stabilizers and the contribution of the hexagonal form in the polymer; e.g. the M.pt. of phenothiazine is about 100 C lower than that of 2-mercaptobenzimidazole, but in the presence of PT there is 2% more of the β-phase.

Table 2 Average contributions of β-form in crystalline phase iPP with MBIM, PT and TPDT

Samples	% Contribution of β-form iPP before thermal ageing	% Contribution of β-form iPP after thermal ageing
iPP + MBIM	6.82	5.94
iPP + PT	8.10	8.39
iPP + TPDT	28.02	25.86

Perhaps the shape of a stabilizer crystal is one of the reasons why the β-form of iPP is formed. As shown in *Table 1* the crystals of compounds which initiate hex PP have the form of plates or needles elongated in the c axis direction and belong to the centrosymmetric space groups. The other reason for the polymorphic transitions may be the molecular structure of the stabilizers. As shown in *Table 2* the higher amount of the β-form in our experiments arises in the presence of PT and TPDT, i.e. in compounds having similar structures in which sulphur atoms are placed above the planes of the phenyl rings[12,14]. It is interesting that Permanent Red E3B,



mentioned above, which also initiates the hexagonal form of iPP, has a similar molecular structure to TPDT[14].

During the thermal ageing (*Table 2*), the amount of α and β forms are unchanged.

The above facts are undoubtedly connected with the observed phenomena, but at this stage of our research it is impossible to determine a close relation between molecular structure and crystal shape of stabilizers and space arrangements of iPP macromolecules during crystallization. This problem is a subject for further investigation.

CONCLUSIONS

The results of the investigations show that polymorphic transitions $\alpha \rightarrow \beta$ of isotactic polypropylene may be caused by small amount of additives (phenothiazine, 2-mercaptobenzimidazol, triphenodithiazine) having M.pt. higher than the polymer.

The contribution of the β-form in iPP depends upon the type of the stabilizer. In the presence of MBIM, PT, TPDT stabilizers, the amount of β-iPP before and after heating is not changed.

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REFERENCES

1 Natta, G. and Corradini, P. *Nuovo Cimento* 1960, **15** 1, 40
2 Keith, H. D. and Padden, F. J. *J. Appl. Phys.* 1959, **30**, 1485
3 Turner-Jones, A., Aizlewood, J. M. and Beckett, D. R. *Makromol Chemie* 1964, **75**, 136

4 Addink, E. J. and Beintema, J. *Polymer* 1961, **2**, 185
5 Dragaun, H., Hubeny, H. and Muschik, H. *J. Polym. Sci. Pol. Phys. Edn.* 1977, **15**, 1779
6 Leugering, H. J. *Makromol. Chemie* 1967, **109**, 204
7 Zuk, A., Garbarczyk, J. and Perkowska, B. *J. Appl. Polym. Sci. Appl. Polym. Symp.* 1979, **35**, 83–88
8 Garbarczyk, J., Zuk, A. and Zmidzinski, F. *Prace z Inzynierii Materialowej, Polit. Pozn.* 1979, 223
9 Dik-Edixhoven, C. J., Schenk, H. and Van der Meer, H. *Cryst. Struct. Comm.* 1973, **2**, 23
10 Form, G. R. and Raper, E. S. *Acta Cryst. (B)* 1976, **32**, 345
11 Mornon, J. P., Bally, R. and Brassy, C. *C. R. Acad. Sc. Paris* 1977, (t) **284**, 779
12 McDowell, J. J. H. *Acta Cryst. (B)* 1976, **32**, 5
13 Poveteva, E., Tsetkina, L. and Kopylov, V. *Kristallografija* 1976, **21**, 312
14 Garbarczyk, J. in preparation