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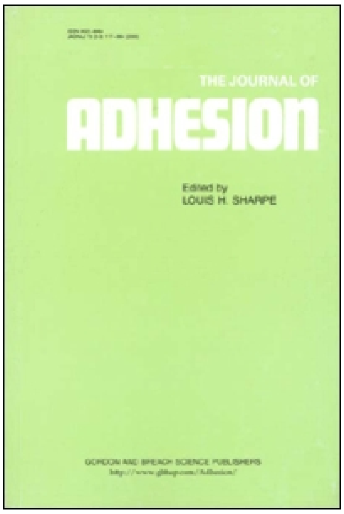

The Journal of Adhesion

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

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To cite this Article Hata, T. , Ohsaka, K. , Yamada, T. , Nakamae, K. , Shibata, N. and Matsumoto, T.(1994) 'Transcrystalline Region of Polypropylene: Its Formation, Structure and Mechanical Properties', The Journal of Adhesion, 45: 1, 125 — 135

To link to this Article: DOI: 10.1080/00218469408026633

URL: http://dx.doi.org/10.1080/00218469408026633

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J. Adhesion, 1994, Vol. 45, pp. 125–135
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Printed in the United States of America

Transcrystalline Region of Polypropylene: Its Formation, Structure and Mechanical Properties*

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(Received November 1, 1992; in final form January 20, 1993)

The question of the dominant factors in the production of a transcrystalline region (TCR), an "interphase," in crystalline polymers on solidifying in contact with a substrate is investigated for isotactic polypropylene (PP) using polarization microscopy and scanning electron microscopy. Several uncoated substrates, and the same substrates coated with certain vacuum-evaporated metals and carbon, as well as surface replicas of these made with cellulose acetate, are compared as nucleating surfaces. It is concluded that TCR formation is not dependent on the species of substrates or their surface energy but on the geometrical morphology or surface roughness. In fact, the rough surface produced by abrasion with carborundum powder creates a TCR for every substrate used. An all-transcrystalline (TC) film of PP more than 300 μm thick is obtained by hot pressing the PP between two sheets of PTFE. Wide- and small-angle X-ray analysis of the film reveals a "cross-hatch" structure of lamellae. Micro-beam X-ray analysis shows that three-dimensional crystal growth occurs up to 20–30 μm from the interface and, thereafter, a one-dimensional TCR grows up to the mid-plane of the film from both sides. The stress-strain behavior of the various TC films are compared with spherilitic-crystalline and quenched amorphous films. The TC film is able to undergo up to 800% elongation in spite of its almost perfect crystallinity. The mechanism of deformation is discussed on the basis of X-ray observations.

KEY WORDS polypropylene; transcrystalline region; crystallization; structure; deformation; TCR; interphase.

INTRODUCTION

It is well known that, when a crystalline polymer is crystallized on some substrate, the highly-oriented crystals grow from the interface, forming the transcrystalline region (TCR). Schonhorn has proposed on the basis of the theory of the weak boundary layer that the reinforcement of the surface layer with the TCR can improve adhesive properties. Polymeric materials having highly-oriented crystalline

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*Presented at the International Symposium on "The Interphase" at the Sixteenth Annual Meeting of The Adhesion Society, Inc., Williamsburg, Virginia, U.S.A., February 21–26, 1993.

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structure such as TCR are very attractive materials since they are expected to show unique behaviors in mechanical properties, diffusivity, permeability, and other properties.

Kwei *et al.*[1] investigated mechanical properties of multi-layered films of polyethylene composed of TCR and the spherulite structure and estimated physical properties of single-layered film of TCR using a composite rule. Recently, we have found that isotactic-polypropylene (PP) film of more than 300 μm in thickness containing only TCR can easily be obtained by interposing PP melts between two sheets of poly(tetra-fluoroethylene) film, followed by cooling at room temperature or isothermal crystallization.

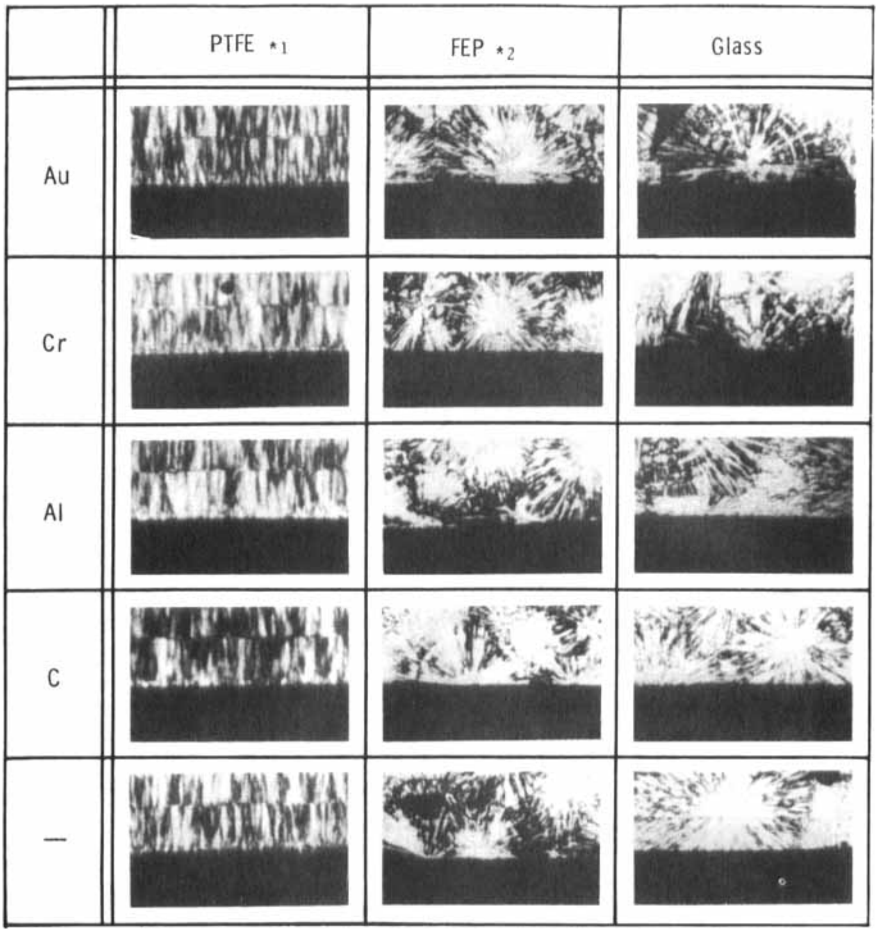
In this study, we investigate morphological structure and mechanical properties of the TC film of PP obtained with this method. In the following sections, firstly, we will examine necessary conditions of surface properties of the substrate for TCR formation and propose a mechanism of the TCR formation. Secondly, one-dimensional crystal growth of TCR will be verified, by comparing the isothermal crystallization process for TCR with that for spherulites. Thirdly, structure of the TCR will be revealed by analysis of X-ray scattering measurements and, lastly, behaviors of elongational deformation of TC film will be compared with those of spherulite film and quenched amorphous film.

FORMATION OF TCR[2]

PP film (Noblen MA-6, Mitsubishi Petrochemical Co.) was interposed between various substrates, pressed and melted at 210°C under the pressure of 5 kg cm^{-2} for 15 min, followed by cooling at room temperature after releasing the pressure.

If the substrates at both sides of the PP film were poly(tetrafluoroethylene) (PTFE), the TCR grew from interfaces of both sides of the film. Crystallization fronts of TCR from the two sides met at the center of film and stopped, forming a "mid-plane" boundary of the two TCR. By this procedure, we could easily obtain PP film made only of TCR. On the contrary, no TCR but only spherulites were formed if other materials were used as the substrate, for example, Al, Cu, brass, glass, poly(ethyleneterephtalate) (PET), and poly(tetrafluoroethylene-co-fluoropropylene) (FEP), whose surface energy is as low as that of PTFE (see Fig. 3). It should be noted that the surfaces of the substrates were cleaned by ultra-sonic cleaning followed by washing with acetone and water and drying, but no treatments which roughened the surface were used. The above results were concluded mainly from polarized optical microscopic (POM) observations.

Similar experiments of melt-crystallization were carried out using the substrates coated with vapor-deposited layers of Au, Cr, Al and C. Three of the substrates used above, PTFE, FEP and glass, were selected as basic substrates. As shown in Figure 1, a TCR was formed on PTFE bearing any of the vapor-deposited films, whereas no TCR was formed on any other substrates coated with any of the materials. To avoid uncertainty about the effect of the surface structure of vapor-deposited layers, surface replicas were made using cellulose acetate and PP was melt-crystallized on the replicas. As shown in Figure 2, the results were the same as



*1 Poly(tetrafluoroethylene)
*2 Tetrafluoroethylene-hexafluoropropylene copolymer

FIGURE 1 Polarized optical micrographs of polypropylene crystallized on substrates coated with vapor-deposited metals.

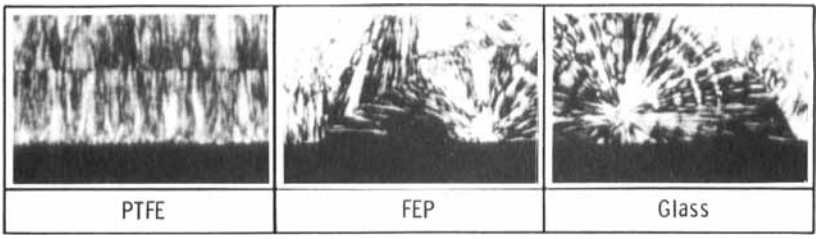


FIGURE 2 Polarized optical micrographs of polypropylene crystallized on replica films.

those for the uncoated substrates. These facts strongly suggest that formation of the TCR does not depend on the material comprising the substrates or their surface energy, but comes from geometrical morphology or surface roughness. In fact, if the surface of the substrates were roughened by using carborundum powder, the TCR was formed on any of the substrates examined. Figure 3 shows scanning elec-

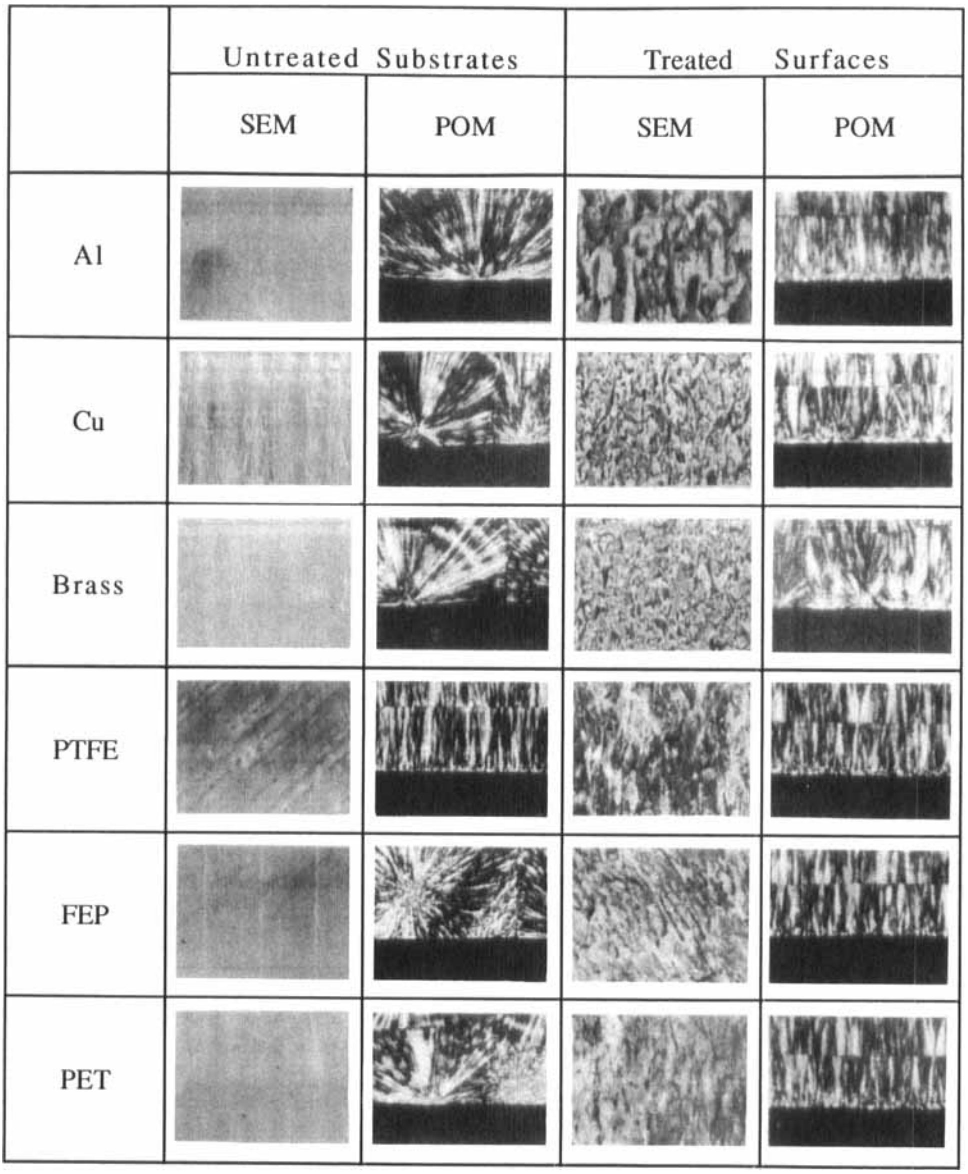


FIGURE 3 Scanning Electron Micrographs (SEM) of the surface of substrates and polarized optical micrographs (POM) of polypropylene crystallized on the substrates indicated. Treated Surfaces: surfaces roughened by carborundum powder.

tron micrographs of the treated and untreated surfaces of several substrates, and polarized optical micrographs of PP crystallized on these substrates.

In conclusion, it has been demonstrated that the dominant factor for TCR formation is the geometrical morphology of the surfaces of substrates. Locally-high energy sites can be nucleation seeds of TC. The presence of so many nucleation seeds being contiguous to each other makes three-dimensional crystal growth difficult and induces crystal growth perpendicular to the interface.

CRYSTALLIZATION KINETICS OF TCR

Kinetics of isothermal crystallization of TCR was investigated by dilatometry. The volume change during the crystallization could be analyzed by the Avrami equation:

$$\log\left(\frac{V_\infty - V_t}{V_\infty - V_0}\right) = kt^n \qquad (1)$$

where t is the crystallization time, V_0, V_t, and V_∞ are the sample volume at $t=0$, t, and ∞, respectively, and k and n are constants independent of t. In the case of three-dimensional growth, n ranges from 3 to 4, which has been supported experimentally. In the case of two- and one-dimensional growths, n is theoretically predicted to be 2 and 1, respectively.

PP samples were prepared by interposing 3 sheets of PP film between 4 sheets of PTFE film. Isothermal crystallization was performed at temperatures ranging from 125°C to 136°C. TC without any other crystals was formed for all cases except the crystallization at 136°C, where a small number of spherulites were observed. For comparison, similar experiments were carried out for the samples prepared without PTFE substrates, where spherulite growth was observed. Avrami plots for spherulite growth and TC growth are shown in Figures 4 and 5, respectively. Avrami plots for the spherulite growth represent a typical behavior of 3-dimensional crystalliza-

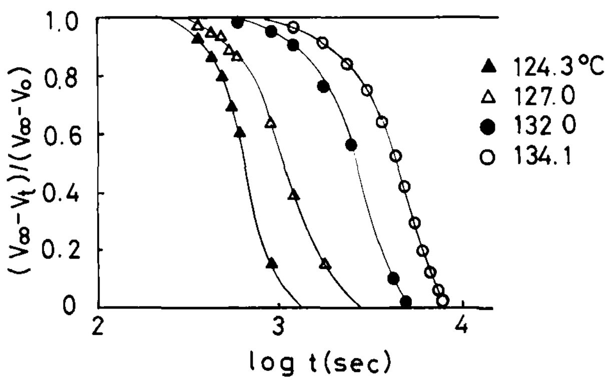


FIGURE 4 Crystallization isothermals of polypropylene crystallized without substrates.

tion. In fact, this plot gave $n \cong 3$. In contrast with Figure 4, one can see from Figure 5 that, in the case of TC growth, the induction period was very short indicating rapid nucleation. One-dimensional growth requires $n = 1$, *i.e.*, the linear relation of $\log [(V_\infty - V_t)/(V_\infty - V_0)]$ and t. This is the case in the crystallization of TC as shown in Figure 6. Hara and Schonhorn[3] obtained $n = 2$ for polyethylene with gold-flake as fillers. In such a system with fillers, nucleation and crystal growth must be heterogeneous, resulting in the coexistence of spherulites and TC. This may be responsible for the deviation from $n = 1$ expected for pure crystallization of TCR.

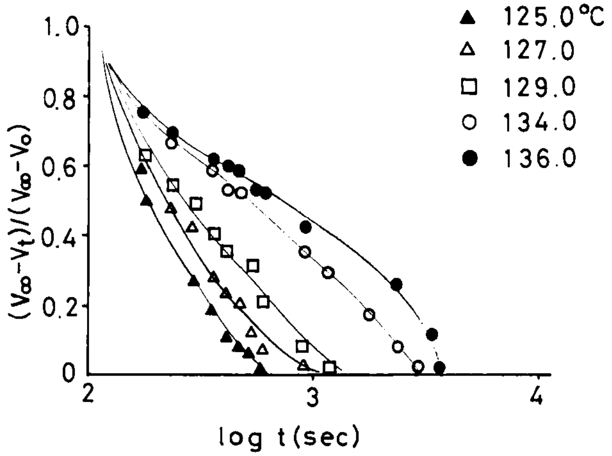


FIGURE 5 Crystallization isothermals of polypropylene crystallized on PTFE.

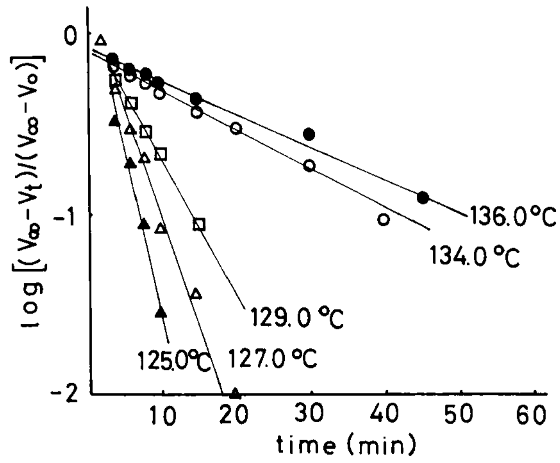


FIGURE 6 Avrami plots for n = 1 for the transcrystalline polypropylene.

STRUCTURE OF TCR

As mentioned in the INTRODUCTION, a TC-film of PP without a spherulite structure was obtained by crystallizing PP-samples interposed between PTFE sheets under cooling or isothermal conditions. We measured wide-angle and small-angle X-ray scattering (WAXS and SAXS) for the samples obtained by cooling at room temperature. Figure 7 shows the wide-angle X-ray diffraction patterns. The diffrac-

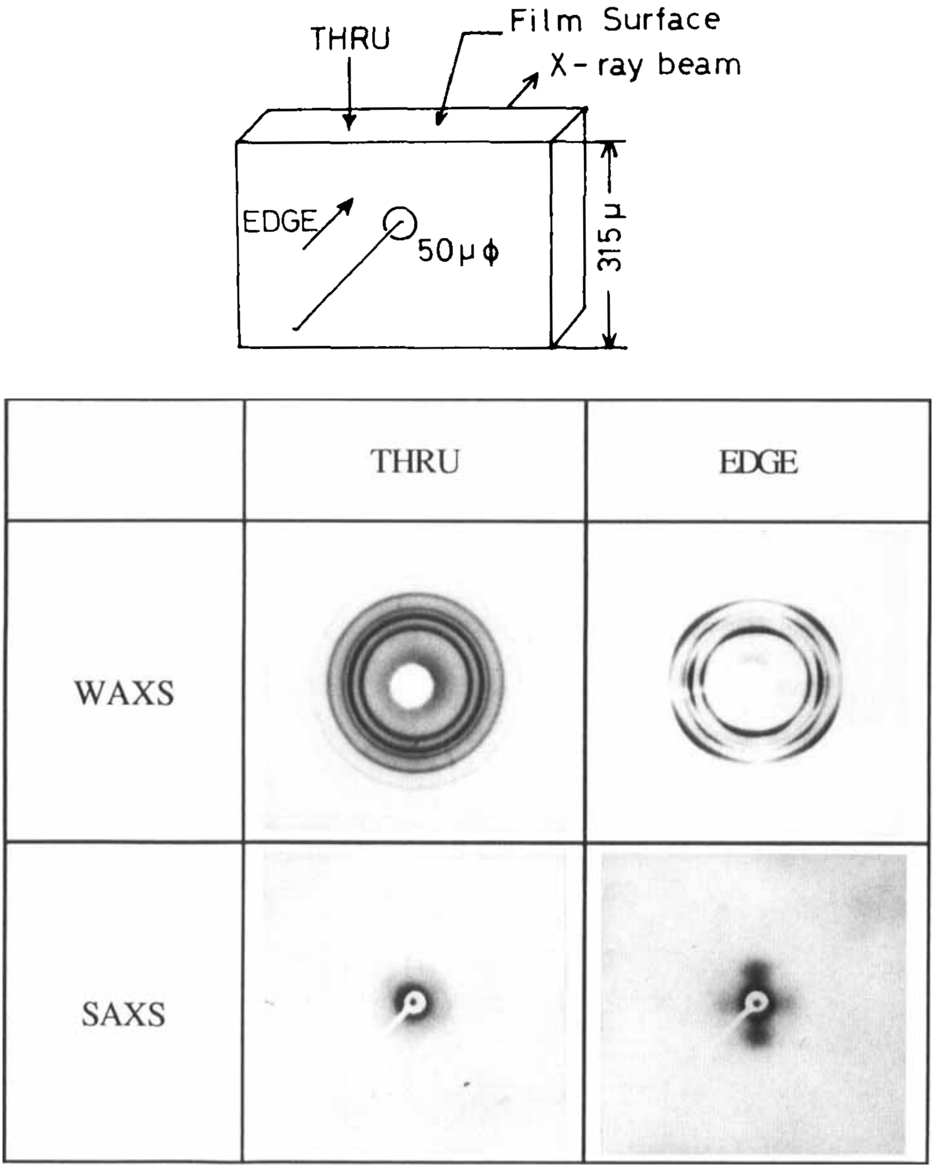


FIGURE 7 X-ray photographs of transcrystalline polypropylene.

tion pattern of the edge view is depicted in Figure 8 along with indexing of reflections. The pattern obtained was identical with the sum of patterns for a*-axis oriented and c-axis oriented crystals. This fact indicates that the TC is a mixture of a*-axis oriented lamellae and c-axis oriented lamellae, having the so-called cross-hatch structure. The diffraction from (040) and (060) planes perpendicular to the b-axis appear on the equatorial line in the edge view, while the diffraction of (040) makes a ring in the through view. Therefore, the b-axis is oriented in the film plane of the TCR.

From the SAXS of the edge view, the long periods of the crystal-growth direction and the direction parallel to the film surface were evaluated to be 190Å and 210Å, respectively. Summarizing all the results mentioned above, we illustrate a model for the structure of TCR in Figure 9.

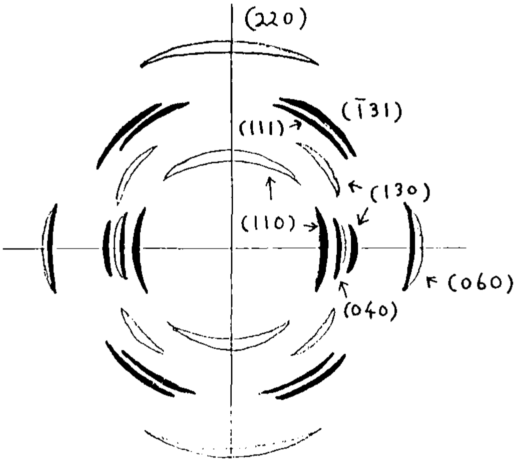


FIGURE 8 Schematic presentation of diffraction patterns for the cross-hatch structure consisting of a*-axis oriented (◡) and c-axis oriented (◒) lamella crystals.

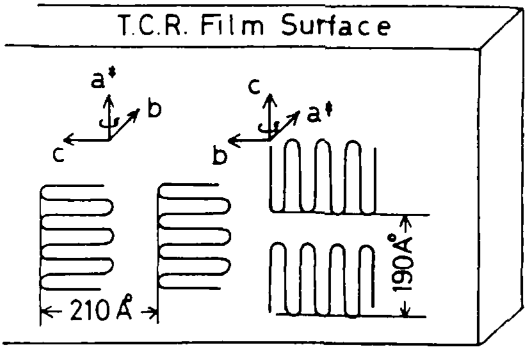


FIGURE 9 Schematic presentation of lamella structure of transcrystalline polypropylene.

The change in the degree of orientation with the distance from the interface was studied by micro-beam X-ray analysis. Diffractions were observed by micro-beam X-ray from the edge direction shining at positions away from the substrate by 10, 30, 40, 75, 125 and 150 μm. At the position of 10 μm, irregularity of orientation was observed in the WAXS pattern which was similar to that of the spherulite film. At the positions of 30 μm and more than 30 μm, the orientational irregularity was not observed. At the present stage, it is not clear whether the orientational irregularity near the interface comes from the surface roughness of substrates or the spherulite-like crystal growth of the nuclei formed at the interface. At any rate, when the crystal grows to 20–30 μm size, it comes into collision with adjacent crystals, is prevented from growing three-dimensionally, and is one-dimensionally oriented in the direction perpendicular to the interface.

STRESS-STRAIN BEHAVIORS OF TC FILMS

Stress-strain behavior of TC-films of PP with a thickness of 315 μm was compared with those of spherulite-crystalline and amorphous films. The spherulite crystalline film was prepared by crystallization on a chromium-coated metal panel under cooling after being hot-pressed at 210°C and 5 kg cm^{-2} for 15 min. The amorphous film was prepared by the same procedure but by quenching into water at 0°C. Load-elongation curves at the elongation rate of 5 mm min^{-1} were measured at 20°C for the films 10 mm in width and 25 mm in length. The TC film was elongated perpendicular to the orientational direction of TCR. The results are shown in Figure 10. Both the initial modulus and the yield stress of the TC film are higher than those of the spherulite crystalline film (see Table I). The spherulite film could be stretched up to 30% at maximum, exhibiting brittle fracture, whereas the TC film could be stretched up to 800% accompanied by the development of opacity and necking. Although 800% elongation is less than that of the amorphous film (1300%), it is a

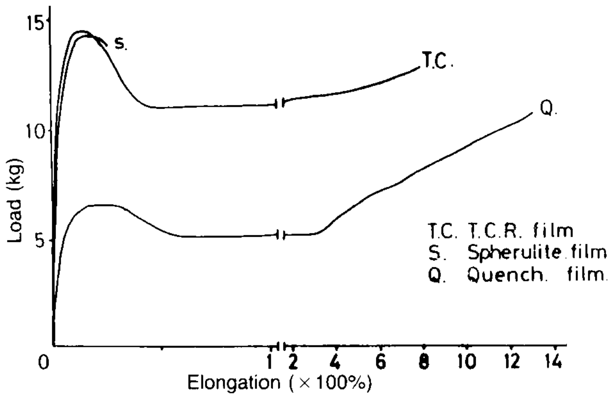


FIGURE 10 Load-Elongation curves for transcrystalline, spherulite-crystalline and amorphous films of polypropylene.

TABLE I
Mechanical properties of transcrystalline, spherulite-crystalline and quenched amorphous films

	TCR film	Spherulite film	Quenched film
Young's modulus (kg/mm^2)	92.5	80.9	36.4
Yield Stress (kg/mm^2)	3.02	2.92	1.38
Yield Point (mm)	3.27–4.50	3.73–5.06	3.82–6.46
Strength at break (kg)	10.40	—	9.09
Elongation at break (%)	789.0	—	1323.0

very unique behavior for crystalline materials with very high degrees of crystallization and orientation.

Figure 11 illustrates a deformation mechanism of the TC film estimated from WAXS and SAXS measurements for the stretched TC film with necking. The a*-axis oriented lamella is declining in the direction of stretching, while the c-axis oriented lamella is being unfolded with stretching. With these changes in structure, micro-voids appear and make the film opaque. The transformation to extended chain crystals by this unfolding process is responsible for the large elongation of TC-film.

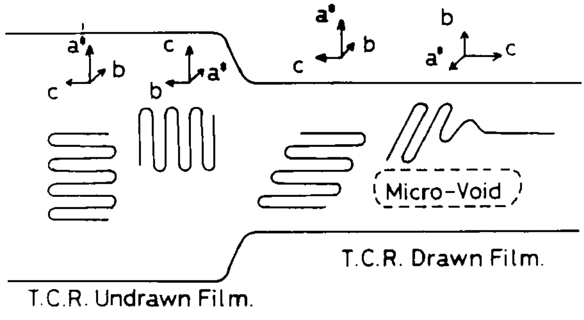


FIGURE 11 Mechanism of large elongation of transcrystalline polypropylene.

CONCLUSIONS

1. Polypropylene formed a TCR by melt-crystallization on PTFE, while it formed spherulites only on other substrates of Al, Cu, brass, glass, PET and FEP. Even on substrates coated with a vapor-deposited layer of Au, Cr, Al and C, and on their surface replicas of cellulose acetate, a TCR could be formed as long as the basic substrate was PTFE, but it was not formed if the basic substrate was any of the other materials. On a rough surface produced by abrasion with carborundum powder, TCR was always formed, irrespective of substrates. From these facts it was concluded that the material species and/or the surface energy of substrates are not factors in TCR formation, but the geometrical morphology or the roughness of the surface is the principal factor.

2. The isothermal crystallization process of TC was investigated by dilatometry. The Avrami index n obtained was unity, which confirmed the one-dimensional crystal growth of TC.
3. X-ray scattering analysis for the structure of the TCR has revealed that the TCR has the so-called cross-hatch structure consisting of two types of lamellae, in which, respectively, the a*-axis and c-axis are oriented perpendicular to the interface. Micro-beam X-ray analysis for the cross section of TC film showed that one-dimensional orientation perpendicular to the interface was realized at 30 μm or further away from the interface, while there existed orientational irregularity up to 10 μm away from the interface.
4. Stress-strain behavior of TC film was compared with those of spherulite-crystalline and amorphous films. The TC film could be stretched up to 800%. A mechanism of elongational deformation of the TC film was proposed, based on the experimental results of X-ray scattering.

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