Polymer Bulletin 43, 75–80 (1999)

Polymer Bulletin

A method for comparing the nucleation ability of PTFE, iPP and sPP on PE

Shouke Yan, Jürgen Petermann

Department of Chemical Engineering, Institute of Materials Science,
University of Dortmund, D-44221 Dortmund, Germany

Received: 29 April 1999/Revised version: 26 June 1999/Accepted: 26 June 1999

SUMMARY

Heterogeneous nucleation is not only a commonly encountered phenomenon of polymer crystallization, but also a fundamentally important research topic for understanding polymer crystallization. Both, polymer epitaxy and transcrystallization are well known mechanisms for surface induced oriented nucleation, but they only have been studied separately with respect to the nucleation abilities of one polymer to another. A new experimental procedure is established to combine transcrystallization and heteroepitaxy of one polymer on two different polymeric substrates. This provides a new way for comparing the relative nucleation onset of one polymer nucleated simultaneously onto two different substrates.

Introduction

Surface induced polymer transcrystallization (1) is a most commonly used method for attesting the heterogeneous nucleation efficiency of one polymer (the substrate polymer) towards another polymer (the deposit polymer). According to the morphologies of the deposit polymer, which are generated by the substrate polymer, the nucleation activity of the substrate polymer can be determined. Systematic studies by optical microscopy equipped with a hot stage have successfully classified the substrate polymers into three categories, i. e. active, moderate and inactive (2-5). But this method can be used only at relatively lower undercoolings since the transcrystallization is hardly be identified at high undercoolings. Moreover, a subdivision of those filled in the same category is impossible.

Heteroepitaxy of polymers is also a well known phenomenon of surface induced polymer crystallization (6-10). Although it has been intensively investigated in the past 15 years, it has not often been used for studying the nucleation ability of the substrate polymer towards the deposit polymer. Therefore, a new experimental procedure combining transcrystallization and heteroepitaxy of one polymer on two different polymeric substrates is established for comparing the relative nucleation onset of the polymer with the two different substrates simultaneously.

The purpose of this paper is to describe the new experimental method and show some illustrative examples of it.

Experimental

As sketched in Fig.1, the experimental set up is performed as follows: On an oriented substrate A, capable for epitaxially crystallizing polymer B, a thin film of polymer B is placed. On top of this double layer, a strip or fiber of a second nucleating material C, which can initiate transcrystallization of the polymer B, is mounted. When crystallizing the polymer B, its morphology in the vicinity of the strip or fiber shaped nucleating material C allows to give very detailed conclusions about the crystallization events. As examples, the sPP(A)/PE(B)/PTFE(C) and iPP(A)/PE(B)/PTFE(C) systems were studied.

The polymers used in this work are isotactic polypropylene (iPP), Novolene 1050FP; high-density polyethylene (PE), Lupolen 6021DX, both from BASF AG Ludwigshafen, Germany; and a commercial grade poly(tetrafluoroethylene) (PTFE). The syndiotactic polypropylene (sPP), having a melting temperature of about 160°C, was supplied kindly by Prof. Dr. Kaminsky of the University of Hamburg, Germany. Uniaxially oriented thin films of iPP, sPP and PE were prepared according to a technique introduced by Petermann and Gohil (11). Highly oriented PTFE strips or fibers were prepared with the help of the friction transfer process (12). The triple layered sample, as shown in Fig. 1, was prepared by mounting a thin film of the crystallizing polymer (B) onto the TEM copper grid which is covered by an oriented thin polymer A film, and then a thin strip of oriented material C was transferred onto this copper grid in the way that material c contacts only with polymer B. The sample was finally heat-treated at 150°C (above the melting temperature of PE but below the melting temperatures of both substrates) for 10min and subsequently quenched to room temperature. For electron microscopy observation, a Philips CM200 TEM operated at 200kV was used in this study. Bright-field (BF) electron micrographs were obtained by defocusing the objective lens.

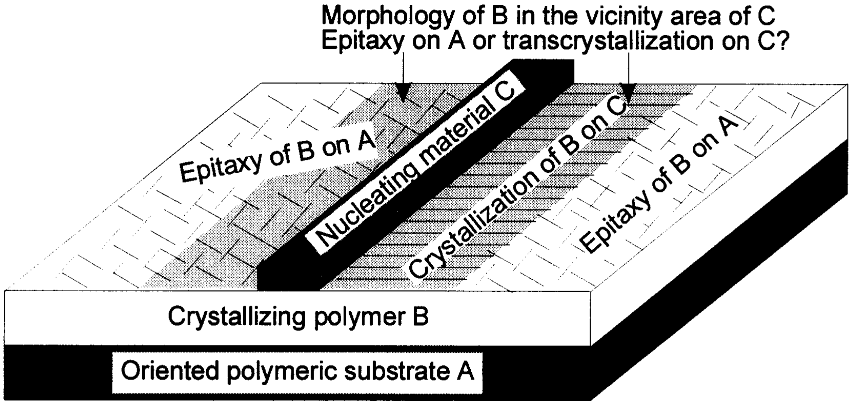

Fig.1 a sketch showing the experimental procedure used in this work

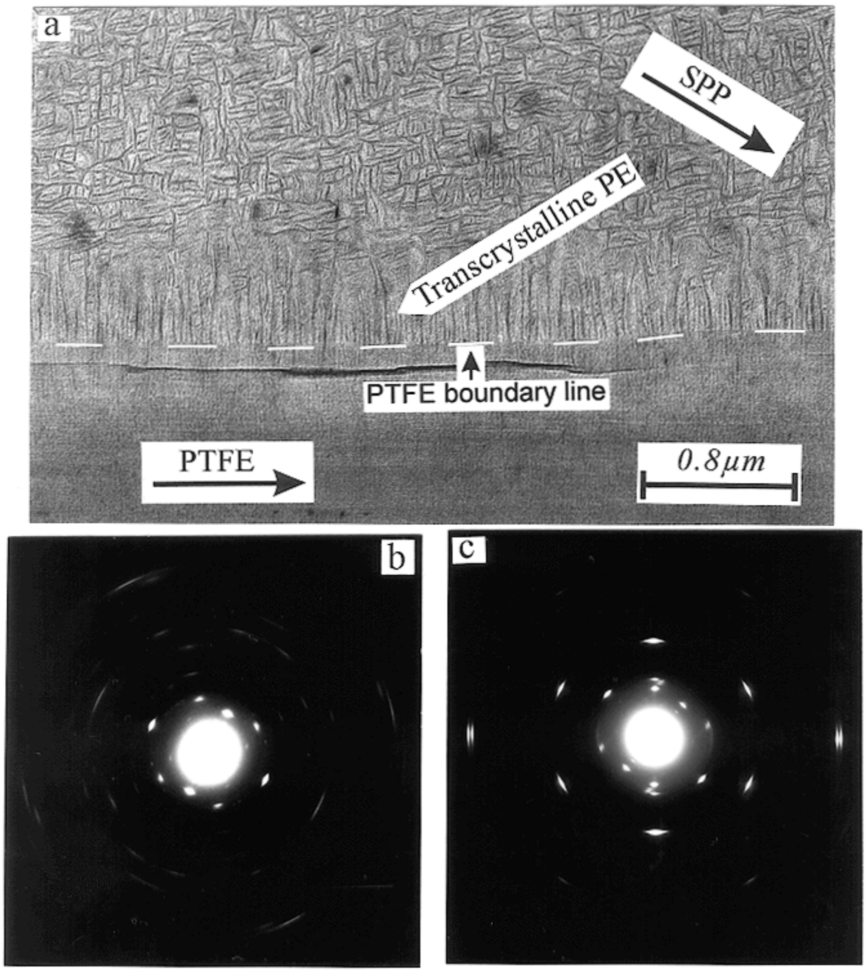

Fig.2 (a) BF image and (b-c) electron diffraction patterns of sPP/PE/PTFE triple layered sample, which was annealed at 150°C for 10min and then quenched to room temperature. The chain direction of sPP is indicated by an arrow labeled with sPP. The PTFE is located in the bottom part of the picture with its chain direction horizontal. The electron diffraction pattern (b) is taken from the upper part where no PTFE exists, while (c) associated to the sPP/PE/PTFE triple layers.

Results and discussion

Fig.2 shows the BF electron micrograph and the corresponding electron diffraction patterns of the sPP/PE/PTFE triple layers, which has been heated to 150°C for 10min and subsequently quenched to room temperature. The arrow labeled with sPP indicates the molecular chain direction of the oriented sPP film. The PTFE substrate is located in the bottom of the BF image (Fig.2a) With its chain direction horizontal as shown by an arrow. On the upper part of Fig.2a, where no PTFE exists, a sPP induced cross-hatched lamellar structure of PE is observed. The corresponding electron diffraction pattern (Fig.2b) taken in this area confirms the occurrence of epitaxial crystallization of PE on the oriented sPP substrate (13, 14). In the boundary area of the PTFE, a transcrystalline zone of PE arises with its lamellae perpendicular to the boundary line of PTFE. This clearly indicates that the PTFE exhibits so strong nucleation power towards PE compared with sPP that a perfect transcrystalline zone of PE forms without any influence of the sPP substrate. In the sPP/PE/PTFE triple layered area, bottom part of the Fig.2a, parallel aligned PE lamellae can be identified when observing the BF image carefully. This demonstrates that the PE sandwiched between the sPP and PTFE substrates crystallizes on the PTFE side. This can also be concluded from the corresponding electron diffraction pattern of this area (Fig.2c). All these evidently indicate that PTFE is more active in nucleating PE than the sPP.

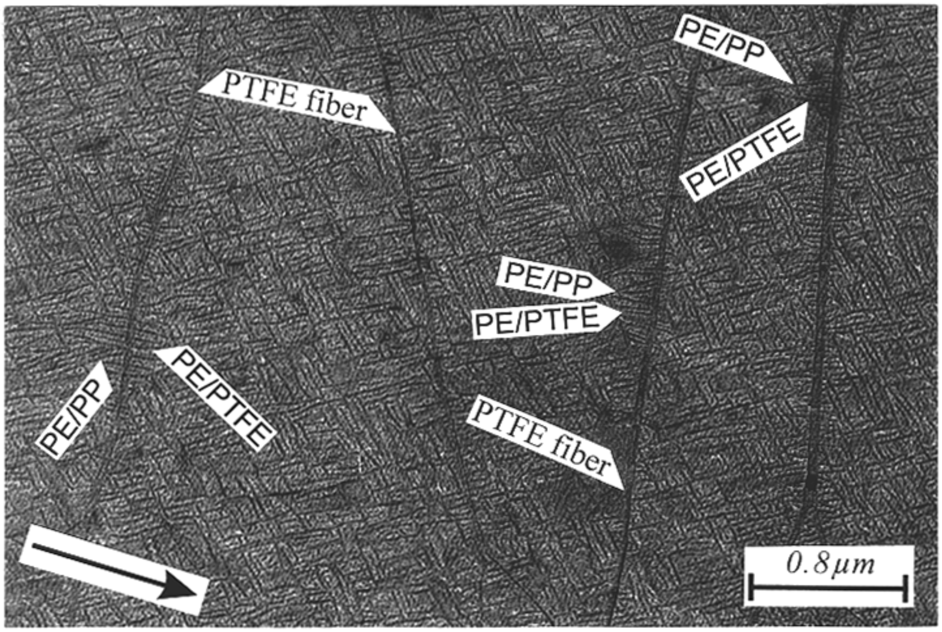

Fig.3 BF electron micrograph of a PE/iPP double layered film with a few PTFE fibers lay on the PE side of the film. The thermal history of the sample is the same as that shown in Fig.2. The arrow indicates the chain direction of the oriented iPP substrate. The white arrows described as PE/iPP and PE/PTFE are used to indicate the PE lamellae which are generated by iPP and PTFE substrates, respectively.

The morphology of PE in the iPP/PE/PTFE system is shown in Fig.3. As indicated, there exist only a few of PTFE fibers dispersed on an even iPP/PE double layered film. The arrow in the picture represents the molecular chain direction of the iPP substrate. Now the PE forms an overall cross-hatched epitaxial lamellar structure generated by the underlying iPP substrate (7, 8). In the vicinity of the PTFE fibers, both epitaxial (as indicated by arrows labeled with PE/PP) and transcrystalline (shown in Fig.3 with the arrows described as PE/PTFE) PE lamellae can be observed. The co-existence of the epitaxial and transcrystalline PE lamellae, even in the same area, implies that the iPP and PTFE have similar nucleation abilities towards PE. This is also confirmed by the electron diffraction pattern of the iPP/PE/PTFE triple layered samples. As shown in Fig.4 with a sketch (Fig.4b), there are totally five reflection sets with high orientation. Among them, one set belongs to the oriented iPP substrate and is illustrated with gray ellipses in Fig.4b. The contribution of the oriented PTFE film is illustrated with the black ellipses. The remaining three reflection sets, as subscribed with I, II and III, are identified as the oriented overgrown PE crystals. The sets I and II are generated by the epitaxial crystallization of PE on the iPP substrate with the c-axes ±50° apart from the chain direction of iPP crystals. The other set, i. e. set III, exhibits the same chain orientation with PTFE, and therefore, reflects the epitaxial overgrowth of PE on the PTFE friction transferred film. According to the results obtained from BF observation and electron diffraction pattern, it can be concluded that the PE crystals are nucleated on the iPP side as well as on the PTFE side, i. e. iPP and PTFE exhibit similar nucleation power towards PE.

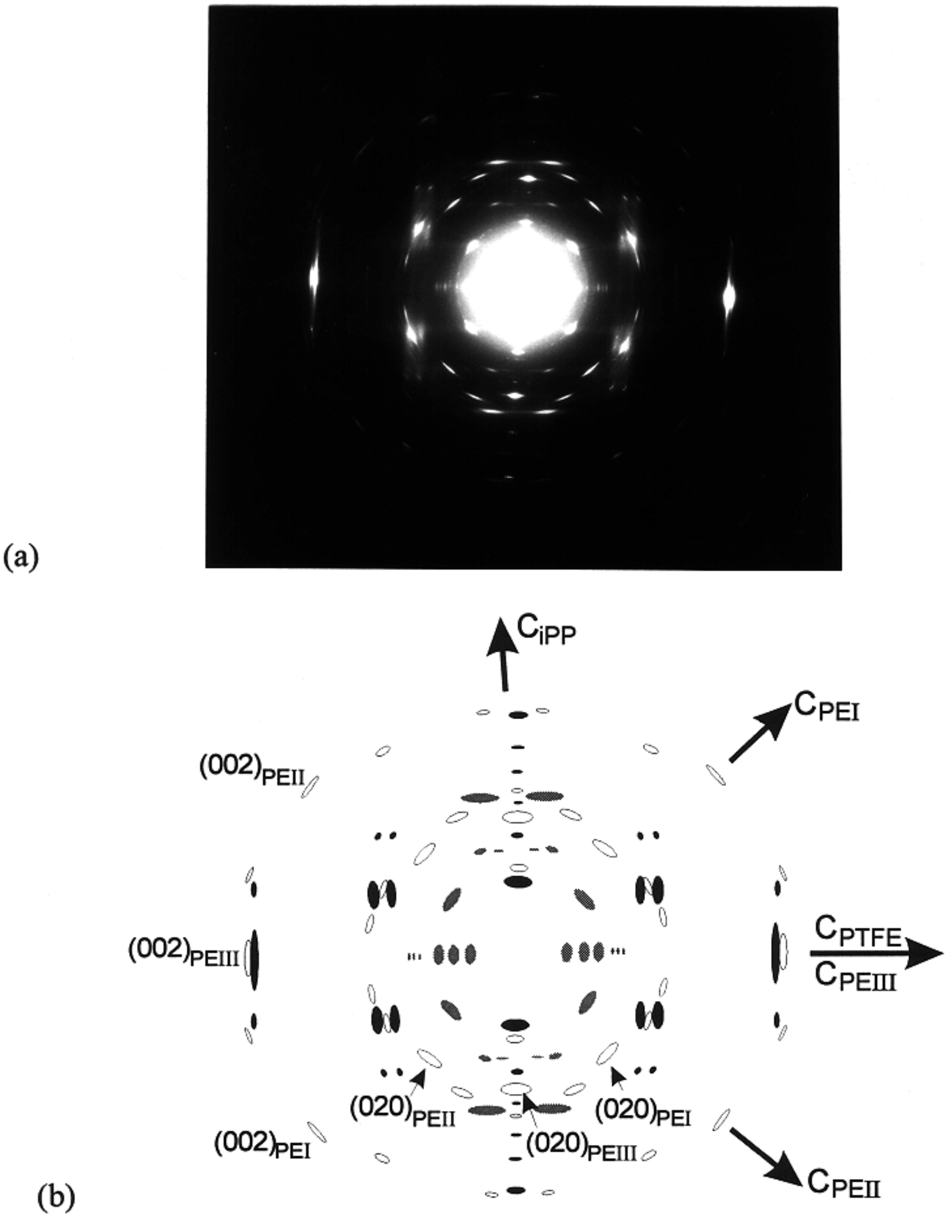

Fig.4 (a) electron diffraction pattern and (b) its corresponding sketch with main reflections being indexed of a sandwich sample with PE embedded between iPP and PTFE substrates. The sample was annealed at 150°C for 10min and then quenched directly to room temperature. The arrows represent the chain directions of the iPP and PTFE substrates, respectively.

According to the above described examples, it is clear that our new experimental set up can be successfully employed to compare the relative nucleation onset of one polymer nucleated simultaneously onto two different substrates. It can be further used to attest the temperature dependence of the nucleation efficiency of different polymers by varying the experimental conditions. For example, cooling the iPP/PE/PTFE multilayers from 150°C with a rate of 5°C/min to room temperature, the PE crystallizes only on the PTFE side (15). This means that at lower undercoolings the PTFE exhibits higher nucleation power than the iPP.

Conclusions

With the new experimental set up, the nucleation efficiency of two different substrate polymers onto one deposit polymer can be directly compared. The results obtained from BF electron microscopic observations and the corresponding electron diffraction patterns of the sPP/PE/PTFE and iPP/PE/PTFE example systems show that PTFE exhibits evidently stronger nucleation ability towards PE than the sPP substrate, while PTFE and iPP show similar nucleation activities onto PE.

Acknowledgment

The financial support of the Deutsche Forschungsgemeinschaft (DFG) and Fonds der Chemiechen Industrie (FCI) are gratefully acknowledged.

References

1. Schonhorn H (1964) J Polym Sci, B2(2): 465
2. Chatterjee AM, Price FP, Newmann S (1975) J Polym Sci, Polym Phys Ed 13: 2369
3. Chatterjee AM, Price FP, Newmann S (1975) J Polym Sci, Polym Phys Ed 13: 2385
4. Chatterjee AM, Price FP, Newmann S (1975) J Polym Sci, Polym Phys Ed 13: 2391
5. Seth KK, Kenpster CJE (1977) J Polym Sci, Symp 58: 297
6. Wittmann JC, Lotz B (1990) Prog Polym Sci 15: 909
7. Petermann J (1995) Epitaxial growth on and with polypropylene. In: Karger-Kocsis J (ed) Polypropylene: Structure, blends and composites. Chapman & Hall, London, pp. 140.
8. Yan S, Yang D, Petermann J (1998) Polym 39: 4569
9. Wittmann JC, Lotz B (1986) J Polym Sci, Polym Phys Ed 24: 1559
10. Yan S, Petermann J, Yang D (1997) Polym Bull 38: 87
11. Petermann J, Gohil RM (1979) J Mater Sci Lett 14: 2260
12. Wittmann JC, Smith P (1991) Nature 352: 414
13. Petermann J, Xu Y, Loos J, Yang D (1992) Polym Commun 33: 1096
14. Schumacher M, Lovinger AJ, Agarwal P, Wittmann JC, Lotz B (1994) Macromol 27: 6956
15. Yan S, Petermann J, J Polym Sci, Polym Phys Ed, submitted