Effect of nucleating agent on the structure development in isotactic polypropylene/liquid paraffin mixture

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We investigated the crystallization behaviour in an isotactic polypropylene (PP)/liquid paraffin (LP) mixture loaded with a small amount of nucleating agent (NA) under a microscope. Three types of crystallization behaviour were observed, depending on the crystallization temperature and the composition: (1) connected nucleation (CN)-type crystallization which yields a unique network structure consisting of interconnected PP crystals; (2) aggregated nucleation (AN)-type crystallization; and (3) the familiar spherulitic crystallization. The CN and AN types were never observed in binary mixtures of PP/LP and PP/NA. In contrast, the NA/LP mixture developed a network structure consisting of highly interconnected axialite-like crystals of NA. The crystallization mechanism in the ternary mixture (PP/LP/NA) was found to be controlled by the competitive kinetics of the NA crystallization *versus* that of PP; e.g., the network structure is created when NA crystallization occurs and then small PP crystals grow densely along the fibrils in the axialite NA crystals.

(Keywords: polypropylene; liquid paraffin; nucleating agent; ternary mixture; crystallization; network structure; gelation; competitive kinetics)

INTRODUCTION

One of the authors found that crystallization under deep quench in an isotactic polypropylene (PP)/liquid paraffin (LP) mixture loaded with a small amount of nucleating agent (NC4) yields a unique network structure with uniform mesh size of *ca.* 1 μm, in which skeleton moiety consists of the interconnected PP crystals[1,2]. By extracting LP after the crystallization, one can prepare a porous membrane with uniform pore size. A potential application for the porous membrane is an artificial lung. Our interest is to clarify the crystallization mechanism which creates the unique network morphology.

In this paper we investigate the crystallization behaviour in the ternary mixture by optical microscopy. We also observe the crystallization in binary mixtures of PP/LP and NC4/LP to obtain supplemental results. In the light of these results, we discuss the kinetic aspects of the crystallization.

EXPERIMENTAL

The PP used was a commercial polymer supplied by Mitsui Toatsu Chemicals, Inc. (J3HG; $M_w = 3.5 \times 10^5$, $M_n = 5.0 \times 10^4$). The LP was supplied by Chuo Kasei Co. Ltd. (350S; $M_w = 435$, $M_n = 427$), and the nucleating agent, 1,3,2,4-di-*p*-ethylbenzylidene sorbitol (NC4), was supplied by Mitsui Toatsu Chemicals Inc.

PP and NC4 were mixed by a mixing extruder (CSI MAX Mixing Extruder, CS-194, Custom Scientific Instruments Inc.) at 200°C (NC4: 0.2 phr) and the extrudate was chopped into pellets. The PP/NC4 pellets were pressed at 200°C into a film or the pellets were dissolved in LP at 200°C to prepare a LP-rich ternary mixture of PP/LP/NC4. To obtain a PP-rich specimen the pellet and LP were mixed using a Mini-Max Molder (CS-183 MMX, Custom Scientific Instruments Inc.). The thin layer specimens (*c.* 40 μm thick) were easily prepared by spreading the ternary mixture between two cover glasses.

The specimen was maintained at 200°C for 1 min, and then the melt was rapidly quenched to a crystallization temperature by using a hot-stage (Linkam TH600 heating-cooling stage, Linkam Scientific Instruments Ltd) set on optical microscope stage. Crystallization behaviour was observed under a microscope (Olympus BH-2) equipped with a TV video recording system.

After LP was extracted from the crystallized specimen with benzene, the texture was observed under a scanning electron microscope (SEM).

NC4/LP solution was made up in a sample tube at 240°C. The solution was quenched in a water bath or silicone oil bath kept at a constant temperature. After standing for 5 min, the test tube was inverted. If the solution was still a transparent fluid with low viscosity, we judged that the solution was a sol. If the solution changed to a viscous fluid and the level meniscus deformed under its own weight, we judged that the solution was a highly viscous sol. When the meniscus could not deform, we judged that the system had gelled. The H_v (cross polarized) light scattering was carried out for the gelled specimen. Immersing the gelled specimen into benzene, LP was extracted. Differential scanning calorimetry (d.s.c.) (910 DSC, Du Pont) measurements for the extracted gel were carried out at a heating rate of 20°C min^{-1}.

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RESULTS AND DISCUSSION

Crystallization behaviour in the PP/LP/NC4 mixture

Various morphologies were found to develop during the crystallization of the ternary mixture of PP/LP/NC4 (NC4: 0.2 phr), depending on the crystallization temperature T_c and PP content. In terms of morphological development, the phase diagram of the mixture is divided into five regimes, as shown in *Figure 1*. In regime A, the familiar spherulite of PP developed ('normal spherulite'). In regime B, the normal spherulite grew, and then crystallization proceeded around the spherulite via a connected nucleation (CN)-type crystallization (see below). In regime C, both the normal spherulitic and the CN-type crystallizations took place simultaneously. In regime D, the CN type occurred all over the system. In this regime, the network structure consisting of interconnected PP crystals developed, as typically demonstrated by a SEM of the extracted specimen in *Figure 2*. In regime E, aggregated nucleation (AN)-type crystallization (see below) occurred.

The early stage of the CN-type crystallization could be observed by the naked eye under microscope but was never recorded as a micrograph due to its extremely weak contrast. This is shown schematically in *Figure 3*. A string-like structure quickly grew and almost simultaneously small crystals grew and lined up on the string-like structure. In regime B, large spherulites appeared and the CN crystallization followed, resulting in a complex morphology (*Figure 4*).

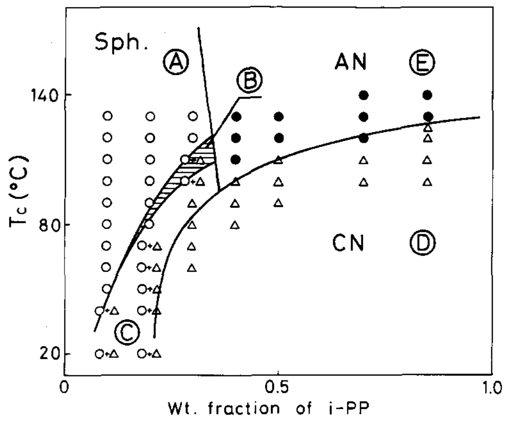

Figure 1 Phase diagram of the PP/LP system (NC4, 0.2 phr) in terms of the structural development. ○ → △, Normal spherulite behaviour and CN follows; △ + ○, CN crystallites and normal spherulites coexist

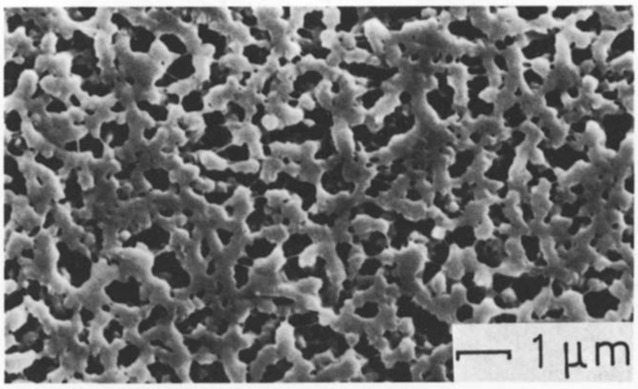

Figure 2 Scanning electron micrograph of the network structure developed in regime D. PP/LP/NC4 = 40/60/0.04 (wt ratio) mixture, crystallized at 40°C, then extracted with benzene

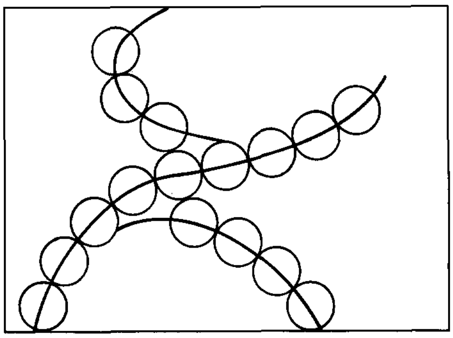

Figure 3 Early stage of connected nucleation (CN)-type crystallization

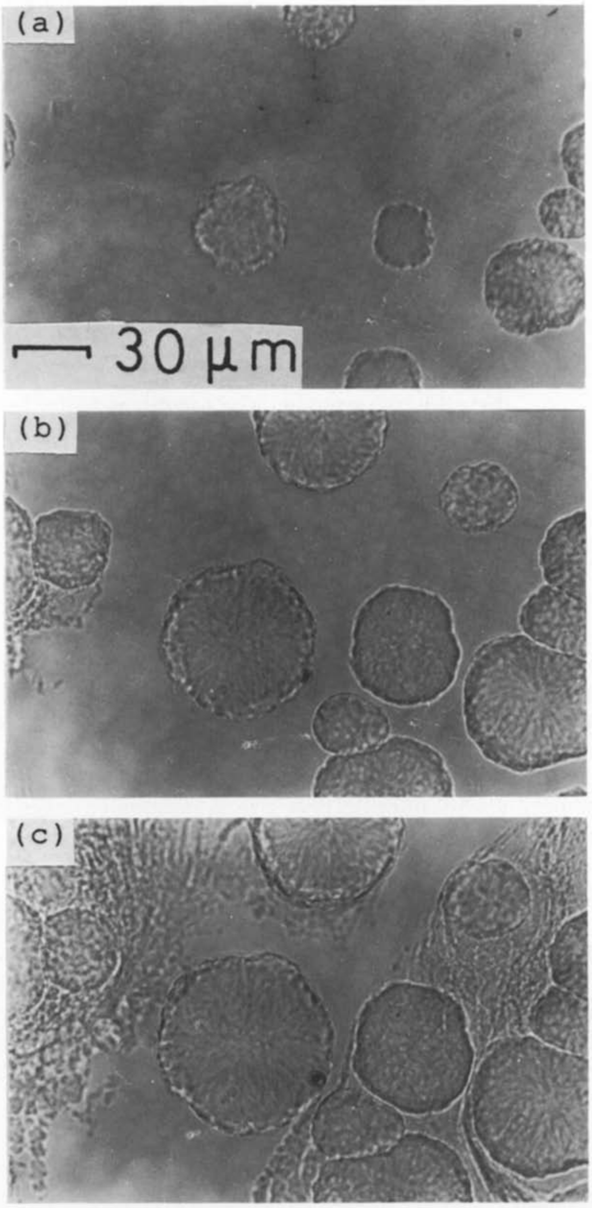

Figure 4 Microscopic observation of the structure development in regime B. PP/LP/NC4 = 30/70/0.06, T_c = 110°C. (a) 1.5 min, (b) 3 min, (c) 4 min

A typical example of the AN-type crystallization behaviour is shown in *Figure 5*. Point-like structures appeared and then assembled in a spherical region (*Figure 5a*). The point-like structures grew and the spherical region increased with time (*Figures 5a* and *b*). Finally, the region was organized into a disordered spherulite (*Figure 5c*).

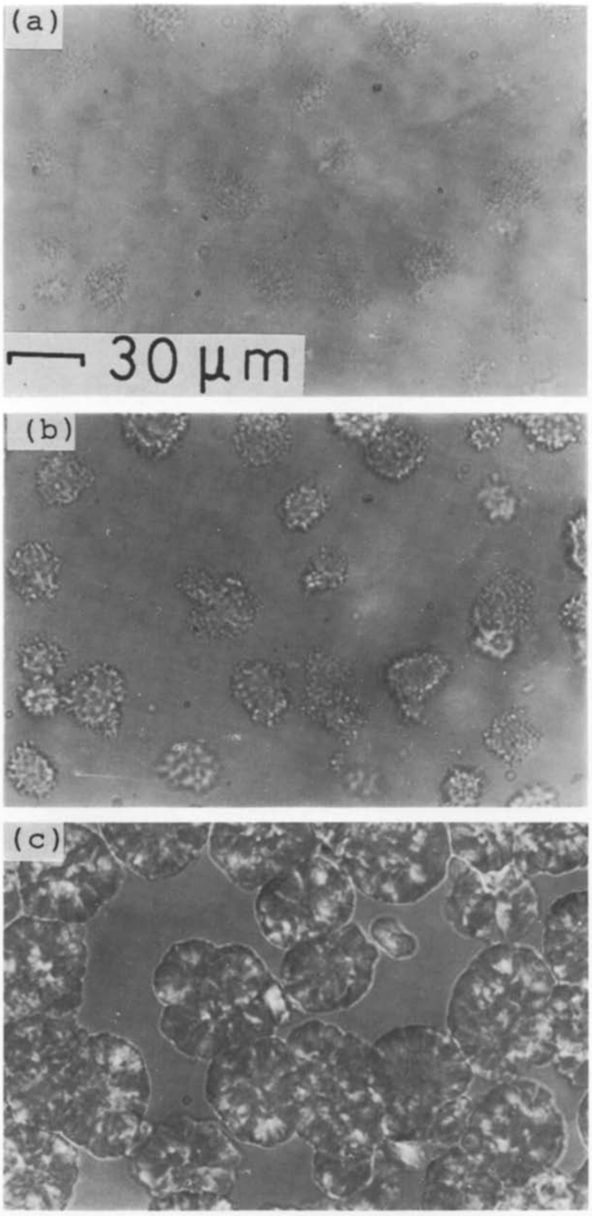

Figure 5 Microscopic observation of the structure development in regime E. PP/LP/NC4 = 70/30/0.14, $T_c = 130$°C. (a) 1 min, (b) 2 min, (c) 20 min

The CN- and AN-type crystallizations were never observed in binary mixtures of PP/LP and PP/NC4. This suggests that the mechanism in the AN- and CN-type crystallizations would be revealed by investigating another binary system of NC4/LP.

Phase behaviour in the NC4/LP mixture

Figure 6 shows the phase diagram of the NC4/LP mixture. The mixture was a transparent sol in regime X, highly viscous sol in regime Y, and a gel in regime Z. As will be discussed later, the high viscosity in regime Y comes from a suspension of axialite crystals of NC4.

A thin film of the gel exhibited the 'rodlike scattering pattern'[3,4] in the H_v light scattering. After extracting LP from the gel with benzene, the residue showed a d.s.c. endotherm peak at 235°C, implying that the residue consists of the crystal of NC4. The microscopic texture of the residue is shown in *Figure 7*. It seems that axialite-like crystals are densely packed and highly interconnected with many branches. We believe that in regime Y the axialite-like crystals are formed, but the population is too small to be interconnected, as shown schematically in *Figure 8a*. This may be the reason why the mixture is a viscous sol in regime Y. The gelation in regime Z is supposed to be as a consequence of the dense interconnection of axialite-like crystals of NC4 (*Figure 8b*).

Crystallization mechanism in the PP/LP/NC4 mixture

Figure 9 is made by overlapping the two phase-diagrams in *Figures 1* and *6*. Note here that NC4 concentration is not proportional to the weight fraction of PP (K) but is roughly equal to $0.2K/(1-K)$. Regime A exists in the sol region (regime X). The AN- and CN-type crystallizations seem to occur in the highly viscous sol region (regime Y) and in the gel region (regime Z), respectively. On the basis of this, we can describe the mechanism of AN- and CN-type crystallization.

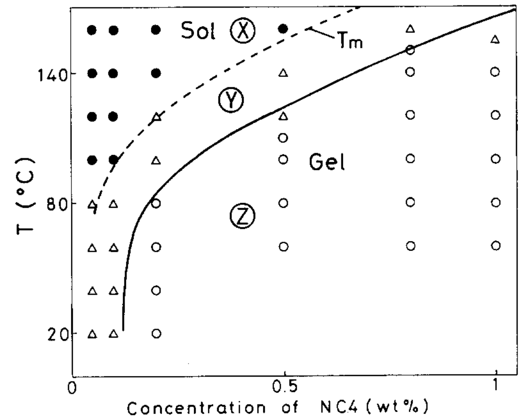

Figure 6 Sol–gel transition (——) and melting temperature (– – –) curves in the NC4/LP system. ○, Gel; ●, transparent sol; △, viscous sol

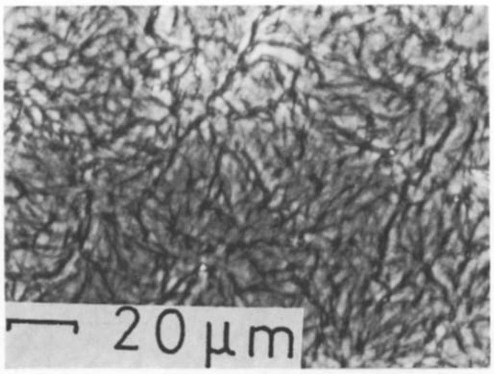

Figure 7 Phase contrast micrograph of an extracted gel. NC4/LP = 3/100, gelled at 180°C

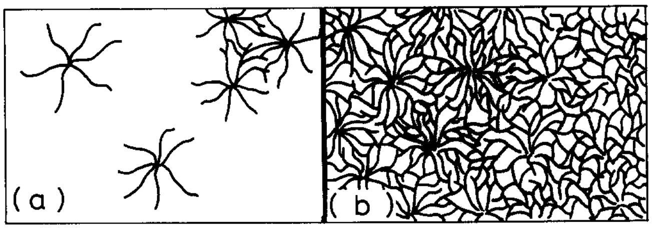

Figure 8 Scheme of textures developed in NC4/LP mixture. In regimes (a) Y and (b) Z

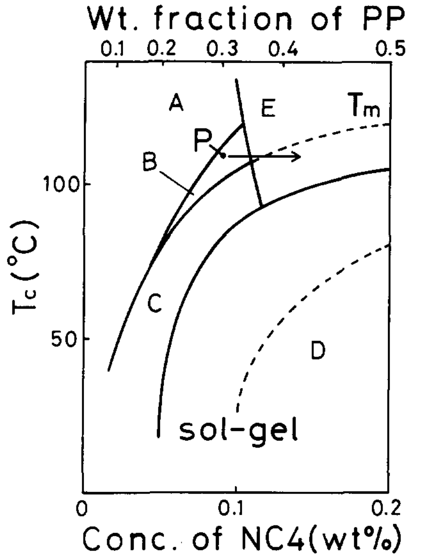

Figure 9 Overlapped phase diagram, from *Figures 1* and *6*

In the AN crystallization, first NC4 crystallizes to form the axialite, as shown in *Figure 8a*, and then PP spherulites grow along the fibrils of axialite crystals of NC4. The crystallization of PP, in this case, proceeds with a relatively low supercooling. Hence, large spherulites appear quite sparsely along the fibrils. This renders the assembled texture under the microscope. The system finally results in the spherical aggregates of small spherulites, as shown in *Figure 5*.

In the CN crystallization, NC4 crystallizes as shown in *Figure 8b*, and then PP crystals grow along the crystal network of NC4. In this case, PP crystallization proceeds under high supercooling. PP crystals grow quite densely along the fibrils, resulting in the interconnected PP crystals coating the NC4 network perfectly and continuously. Thus we believe that the morphological difference between AN and CN is caused by the differences in the continuity of NC4 crystals and the nucleation probability in the crystallization of PP.

Furthermore, in regime B where PP spherulites appear prior to the crystallization of NC4, the spherulite growth would induce a concentration gradient near its growing front, because the spherulite excludes impurities (LP and NC4)[5,6]. When the local concentration of NC4 around the spherulite exceeds the critical one by continuous exclusion (see point P and arrow in *Figure 9*), NC4 will begin to crystallize into fibril-like crystals. Then PP crystallization will proceed along the fibrils and eventually result in the complex morphology shown in *Figure 4*.

The crystallization behaviour in regime B supports the theory that the crystallization mechanism in the PP/LP/NC4 mixture is controlled by the competitive kinetics of the NC4 and PP crystallizations in LP.

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