Investigation of Conditions of Spherulite Formation in Mixtures of Crystalline and Amorphous Polymers

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Synopsis

The supermolecular structure of mixtures of crystalline polymers (low pressure and high pressure polyethylene, isotactic polypropylene) with an amorphous polymer (atactic polypropylene) from the point of view of the influence of the amorphous component on the morphology of the crystalline component has been investigated. The criterion of changes in the morphological state of larger supermolecular formations was the microscopic image of the samples obtained with an optical microscope, both between crossed nicols and in phase contrast. It has been established that the formation of typical spherulites depends on the amount of admixture of the amorphous polymer and also on the treatment of the samples. Upon crystallization in presence of a small amount of solvent (p-xylene), formation of typical spherulites of the crystalline component of the mixture can be observed while the same mixture in case of evaporation of the solvent presents a granulated refractive structure without typical spherulites, regardless of the rate of cooling. The probable role of the solvent is to facilitate mutual segregation of the microphases of both polymers in consequence of decrease in viscosity of the mixture. It has been further shown that even after briefly heating the mixture to a temperature of 220°C., before crystallization, spherulites do not form; on the contrary, spherulites originally present disappear and a structure consisting of smaller refractive formations of crystalline polymer is obtained. The formation of this structure, emerging after destruction of spherulites, might be attributed to an increase of interpenetration of both polymers and to an increase of the contact surfaces between components of the mixture.

The formation of distinguishable spherulites of crystalline polymers is influenced by many factors, the most significant of which are crystallization temperature and the presence of other substances. Since in most cases mixtures of two polymers are immiscible, it can be supposed that the extent of influence on crystallization of a polymer in mixture with an amorphous one will depend also on the miscibility or segregation of the two polymers.

The purpose of this work was investigation of the influence of the addition of an amorphous polymer on the formation of typical spherulitic structures of crystalline polymers of different chemical composition or tacticity.

EXPERIMENTAL

Atactic polypropylene was purified by precipitation from acetone solution; isotactic polypropylene was purified by extraction with boiling

n-heptane. High-pressure and low-pressure polyethylenes were commercial products.

The following mixtures were prepared: low-pressure polyethylene + atactic polypropylene (series A); isotactic polypropylene + atactic polypropylene (series B); high-pressure polyethylene + atactic polypropylene (series C) with weight per cent proportions of 80/20 (samples A_1, B_1, C_1) and 90/10 (samples A_2, B_2, C_2) in each lot.

The method of preparation of thin layers of mixtures of the above series from a 1% solution in p-xylene was identical for all series. The solutions were spread with a glass rod on thin (0.10 mm.) glass plates resting on a metal plate heated to 135 ± 2°C. In preparation method I, the produced film was quickly cooled, immediately after being spread (within ca. 15 sec.) by putting on another metal plate at room temperature while in another method (method II) the samples were kept on the heated plate for about 10 min. with subsequent quick cooling as in method I. All samples were prepared by both methods. Methods I and II of applying the mixture in the form of a p-xylene solution furnished samples having a thickness of 10–15 µ which were suitable for microscopy.

For the different polymers and their mixtures, the temperature intervals in which the reversible disappearance and reappearance of refractive morphological regions could be produced on gradual heating and cooling, respectively, were determined by means of a microscope with a heated plate and the use of polarized light. The rate of heating and cooling in the measured intervals was 0.25°C./min. On the basis of the determined temperature intervals the different polymers and their mixtures were conditioned as follows.

(1) The samples were kept for 10 min. on a hot plate preheated to a temperature about 20°C. higher (with polyethylene and samples C_1, C_2 45°C. higher) than the measured temperature interval in which complete disappearance of crystalline formations was observed, i.e., for samples B_1, B_2, and isotactic polypropylene, to a temperature of 180 ± 3°C.; for samples A_1, A_2, C_1, C_2, high-pressure polyethylene, and low-pressure polyethylene, to a temperature of 150 ± 1.5°C.

(2) The samples were subsequently cooled (approximately 1°C./min.) to a tempering temperature in the range of the temperature interval in which refractive formations reappeared upon decrease of temperature, for samples B_1, B_2, and isotactic polypropylene to 145 ± 1.5°C.; for samples A_1, A_2, and low-pressure polyethylene to 122 ± 1.5°C.; for samples C_1, C_2, and high-pressure polyethylene to 95 ± 1.5°C. The tempering time was 2 hr. for all samples.

(3) The samples were then further cooled at an average cooling rate of 0.5°C./min. down to laboratory temperature.

The microscopic image of the samples obtained with a light microscope (Lumipan, Zeiss) by observing the samples both between crossed nicols and in phase contrast was regarded as the criterion of the influence of the amorphous component on the crystallization process of the other polymer

in the mixture and of morphological changes of larger supermolecular crystalline structures. The photography was carried out in polarized light and in phase contrast with a direct magnification of 145×.

RESULTS

Determination of Temperature Intervals for Polymers and Their Mixtures

By following the effect of temperature on supermolecular crystalline structures suitable for microscopy it was established that upon an increase in temperature they disappeared in a determinate temperature interval ΔT_m. Upon cooling, spherulites suitable for microscopy, as observed in the temperature interval ΔT_c reappeared.

Data on the temperature intervals ΔT_m, ΔT_c of the different polymers and their mixtures are summarized in Table I.

TABLE I

	Composition, wt.-%	ΔT_m, °C.	ΔT_c, °C.
Low-pressure polyethylene + atactic polypropylene	80/20	125–126	120–118
	90/10	126.5–127	122.5–120.5
Isotactic polypropylene + atactic polypropylene	80/20	161.5–162.5	144–140
	90/10	162.5–163.5	146–143
High-pressure polyethylene + atactic polypropylene	80/20	101–102	96–95
	90/10	102–103	97–96
Low-pressure polyethylene		126.5–127.5	123–121
High-pressure polyethylene		105–106	104–103
Isotactic polypropylene		162–164	149–146

Investigations of the Morphological State of a Mixture of Two Polymers

In these experiments mixtures of polymers differing in crystallinity of components were investigated.

The mentioned mixtures of high-pressure polyethylene with atactic polypropylene in various proportions (90/10, 50/50, and 10/90) were investigated in order to establish approximately if and to what extent the proportion of the components affects the morphological state. The samples were prepared according to method I described previously.

Microscopical observations (Fig. 1) showed that admixture of the amorphous component limits the formation of larger spherulites. In descending concentration series with 50/50 concentration of the crystalline component no more marked supermolecular structures were forming. In view of the fact that we were following the morphological state of the mixture by observing it with an optical microscope, higher concentrations of the crystalline component were more suitable. The lowest concentration
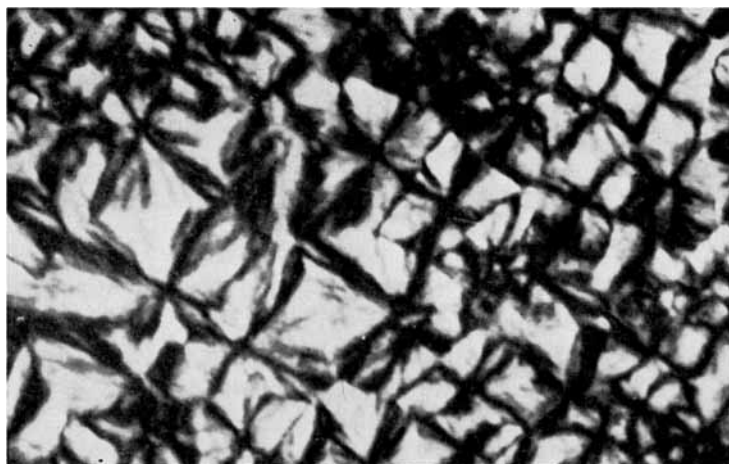
(a)

(b)

Fig. 1.   See caption, p. 503.

of the crystalline polymer in the tested concentration series (10/90) when examined between crossed nicols in the same region observed with the optical microscope showed only sporadic refractive formations /Fig. 1c).

In another experiment on samples of series C only higher concentrations of the crystalline polymer (80/20 and 90/10, i.e., samples C_1 and C_2, and high-pressure polyethylene were used, and the samples were prepared by method II.   On microscopic examination of these samples it was established that there were large morphological formations typical of thin layers and
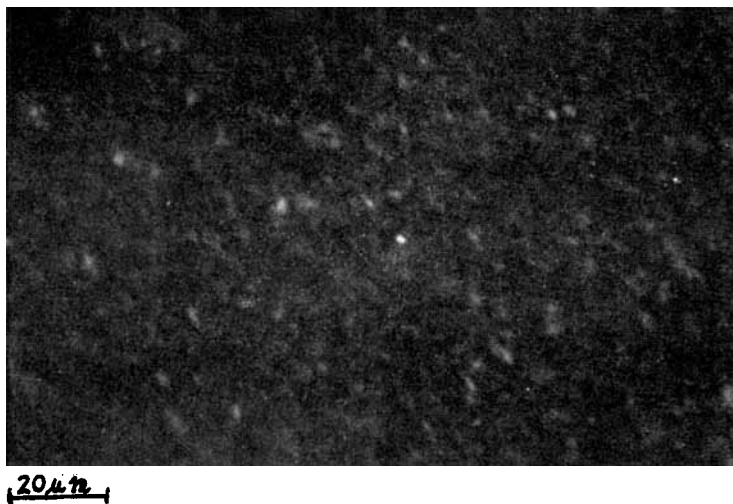
(c)

Fig. 1. Microphotographs between crossed nicols of samples of mixtures of high-pressure polyethylene and atactic polypropylene in different proportions: (a) 90/10 (by weight); (b) 50/50; (c) 10/90. Samples prepared according to method I. Magnification 750×.

that the crystalline component formed more uniform anisotropic morphological structures (Fig. 2).

In order to determine the influence of conditioning on the interaction of the components in the mixture, samples of series C and of high-pressure
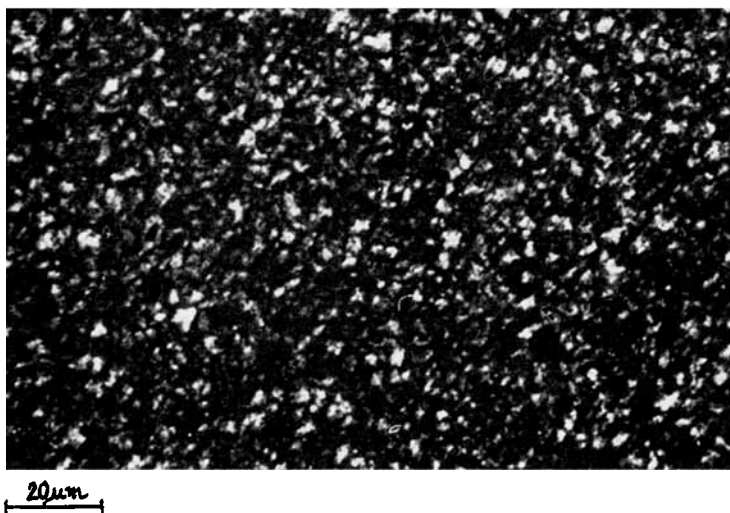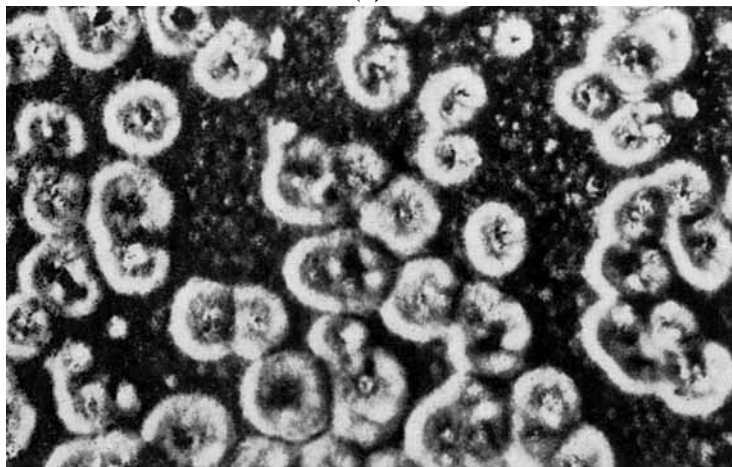

Fig. 2. Microphotographs between crossed nicols of mixture of high-pressure polyethylene and atactic polypropylene (90/10 by weight) prepared according to method II. Magnification 750×.
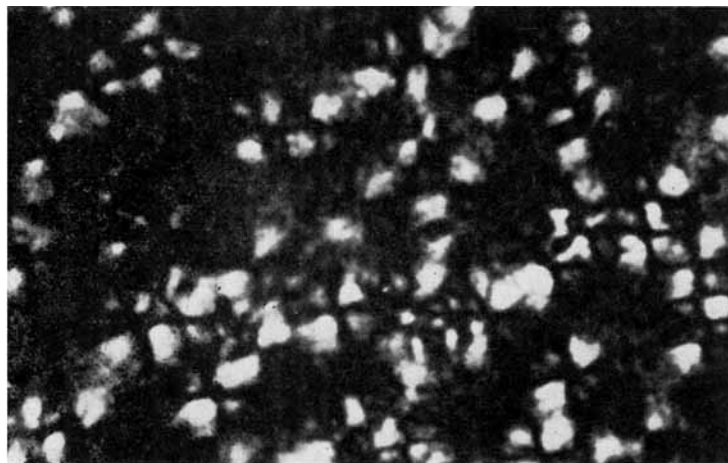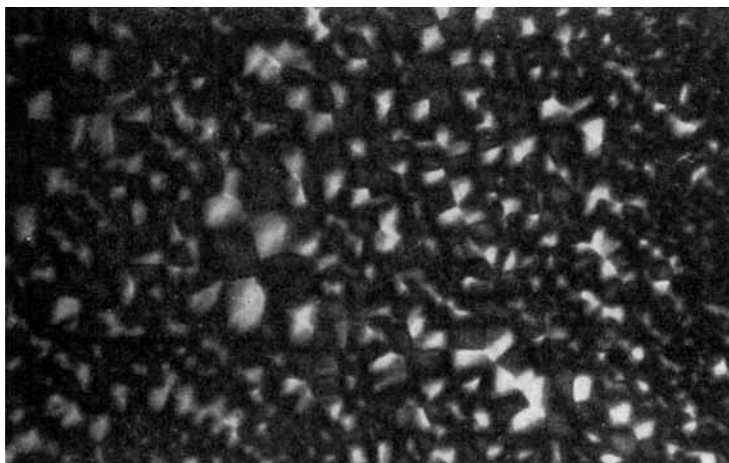
(a)

(b)

Fig. 3. Pair of microphotographs of the same place in sample A₁ (low-pressure poly-ethylene + atactic prolypropylene, 80/20): (a) between crossed nicols; (b) phase contrast. Magnification 750×.

polyethylene were prepared by both methods (I and II), and subjected to the method of conditioning described in detail in the Experimental Section. The results of microscopical analysis after conditioning provided the same morphological image as in the case of method II (Fig. 2).

Samples of series A and B and samples of low-pressure polyethylene and isotactic polypropylene were treated in the same way, i.e., they were prepared in concentrations of 80/20 (samples 1) and 90/10 (samples 2) by both methods and they were subjected to conditioning.
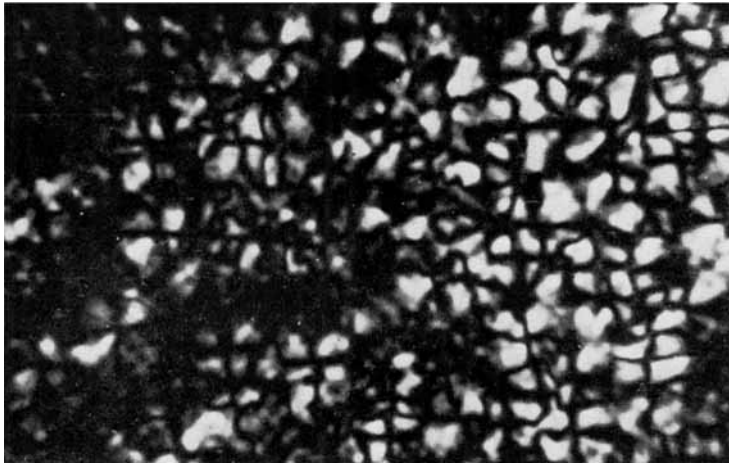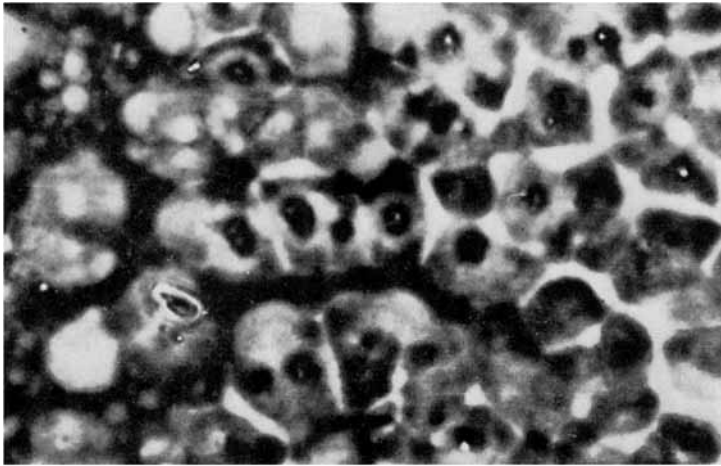
(a)
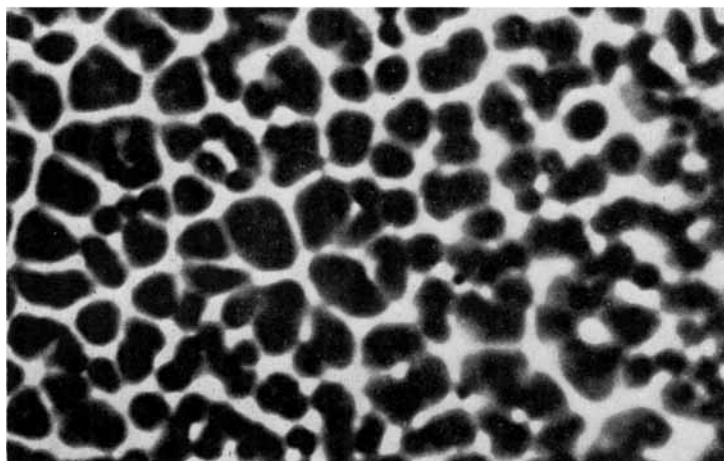
(b)

Fig. 4. Pair of microphotographs of the same place in sample A₂ (low-pressure poly-ethylene + atactic polypropylene, 90/10): (a) between crossed nicols; (b) phase contrast. Magnification 750×.

The microscopical analysis was carried out both after treatment according to methods I and II and after conditioning. The conclusions from these analyses can be summed up as follows.

In all samples, in crystalline polymer as well as in mixtures with atactic polypropylene, after treatment by method I there were formed well developed, supermolecular structures: spherulites typical of thin layers and manifesting in mixtures the morphological characteristics of the basic crys-
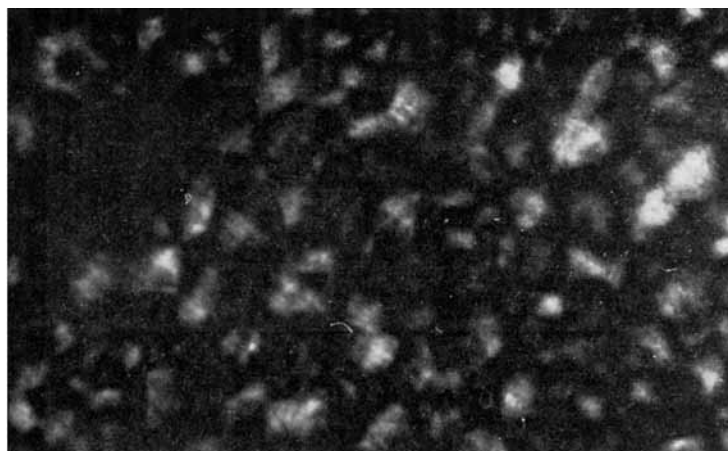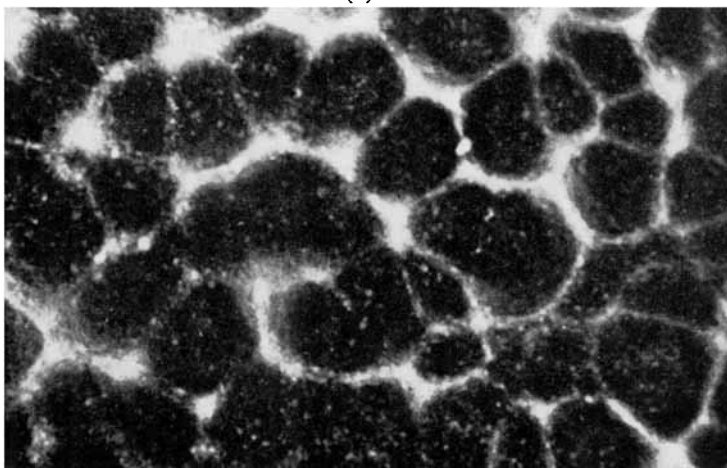
(a)

(b)

Fig. 5. Pair of microphotographs of the same place in a sample of low-pressure poly-
ethylene: (a) between crossed nicols; (b) phase contrast.

talline polymer.   This was verified by microscopical observations for sam-
ples treated by method I.   The morphological state is shown by the figures.
For samples A_1, A_2 (Figs. 3 and 4), low-pressure polyethylene (Fig. 5),
samples C_1, C_2 (Figs. 6 and 7), and high-pressure polyethylene (Fig. 8)
pairs of microphotographs were taken of the same place in the sample both
between crossed nicols and in phase contrast.   Microphotographs taken
between crossed nicols only are shown for samples B_1, B_2, and isotactic
polypropylene (Fig. 9).   In these samples there were mostly only separated

(a)

(b)

Fig. 6. Pair of microphotographs of the same place in sample C_1 (high-pressure poly-ethylene + atactic polypropylene, 80/20): (a) between crossed nicols; (b) phase contrast. Magnification 750×.

spherulites, so that the image in phase contrast supplied no essentially new morphological details (for instance, contact areas between spherulites).

In all samples prepared according to method II, apart from series B, the typical spherulites disappeared, and there were formed morphological structures which showed under the microscope between crossed nicols a more extensive "interpenetration" of crystalline and amorphous components of the mixture.
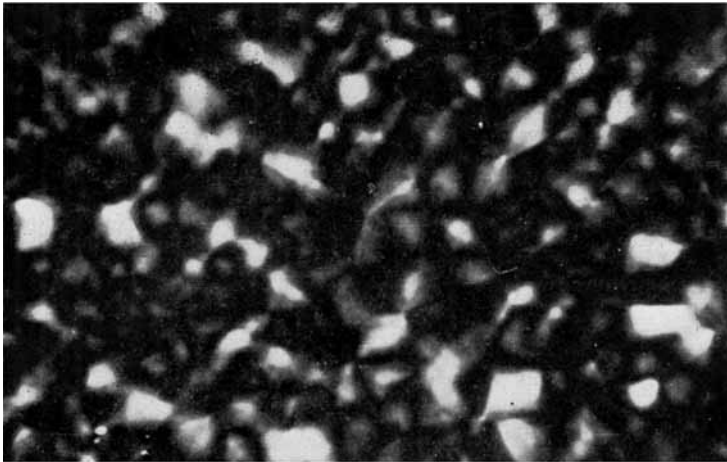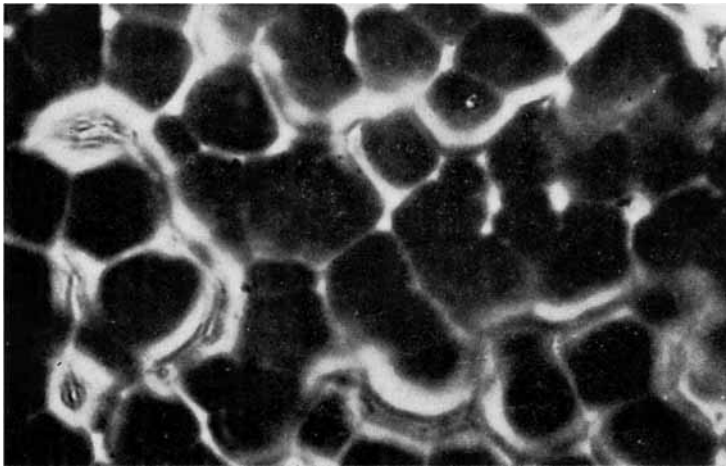
(a)

(b)

Fig. 7. Pair of microphotographs of the same place in sample C_2 (high-pressure poly-ethylene + atactic polypropylene, 90/10): (a) between crossed nicols; (b) phase contrast. Magnification 750×.

In samples of series B (atactic polypropylene and isotactic polypropylene) when method II was used, the large spherulites did not disappear completely and there were formed numerous smaller spherulites corresponding to iso-tactic polypropylene. It seems that a lower admixture of atactic poly-propylene to isotactic polypropylene does not essentially influence the morphological state of the crystalline polymer under the described condi-tions of preparation.

(a)
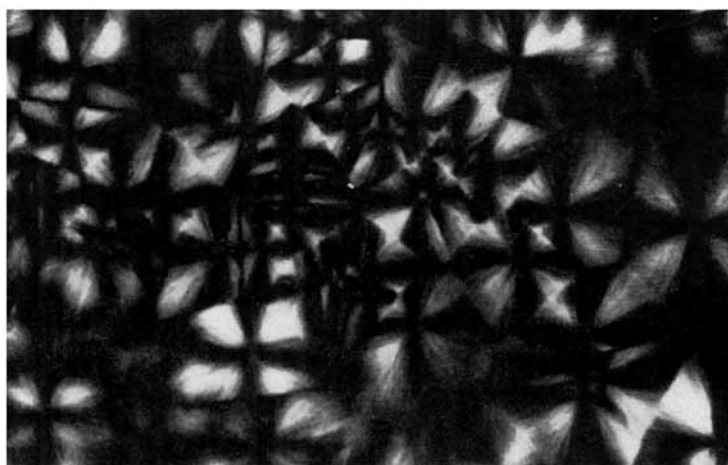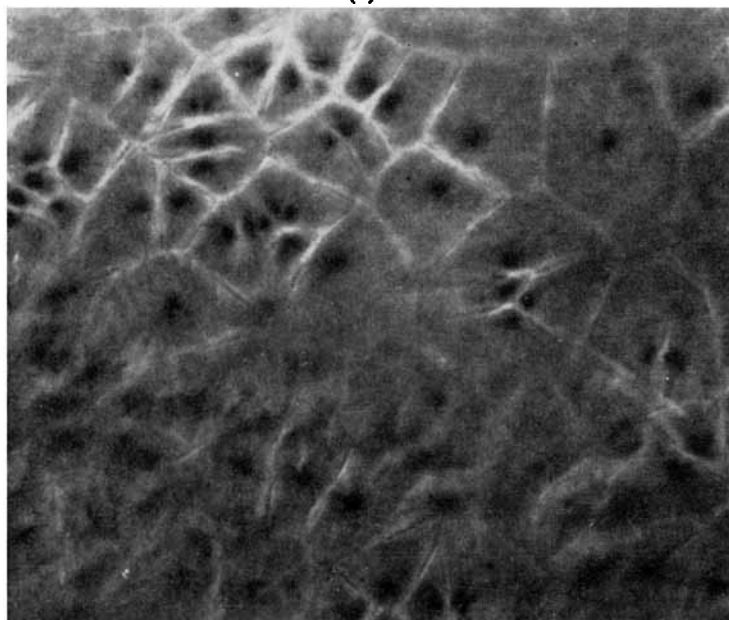
(b)

Fig. 8. Pair of microphotographs of the same place in a sample of high-pressure poly-
ethylene: (a) between crossed nicols; (b) phase contrast.   Magnification 750×.

All samples subjected to prolonged conditioning subsequent to methods
of preparation I and II showed identical morphological images.   It can be
concluded from this that the applied regime of conditioning caused micro-
scopical defects of the spherulites formed by method I.   Samples prepared

(a)
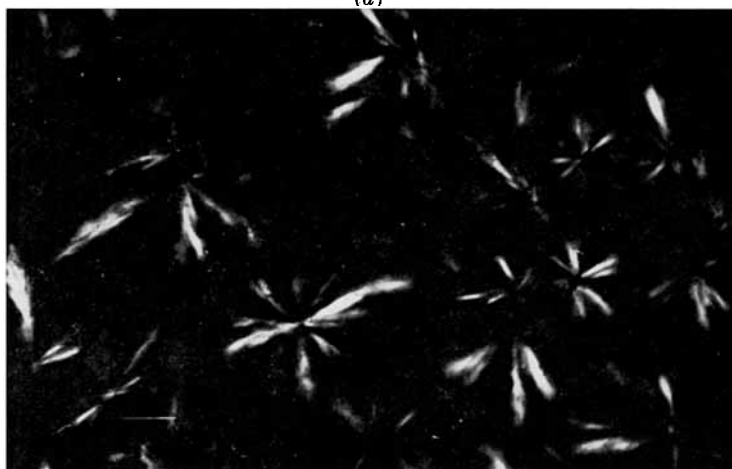
(b)

Fig. 9. See caption, p. 511.

according to method II were not subject to further changes in morphology, not even to growth of spherulites. This means that conditions of interpenetration of both components of the mixture have not changed under the given observation conditions.

DISCUSSION

The formation of regular spherulitic structures of homopolymers usually requires a particular method of sample preparation. Though upon crystallization of the polymer in block granulated structures displaying bire-

(c)

(d)

Fig. 9. Microphotographs between crossed nicols of: (a) sample B_1 (isotactic poly-propylene + atactic polypropylene, 80/20):   (b,c) sample B_2 (isotactic polypropylene + atactic polypropylene, 90/10);   (d) isotactic polypropylene.   Magnification 750✕.

fringence are formed the differentiation of spherulites is impossible.   The formation of these granulated structures can be observed also in polymer films having a thickness of 1–10 μ.[1]   Easily distinguishable spherulites are formed, for example, upon brief heating of a thin layer of polyethylene in the presence of atmospheric oxygen to temperatures 100–200°C. higher than the melting point.[2]   Under these conditions, partial oxidation and degradation of polyethylene occurs, as is evident from the infrared spectra and the molecular weights.[2]   The presence of atmospheric oxygen is proba-

bly the necessary prerequisite for formation of distinguishable spherulite structures. In vacuum only granulated structures are obtained.[2] Since granulation is related to density of nucleation, special attention was given to the possibility of influencing the density of nucleation, particularly by microheterogeneous admixtures in the melt or microheterogeneities on the surfaces of the microscope slides between which crystallization is usually carried out. However, the question of this influence on nucleation density seems to be controversial.[1]

There is considerable evidence for the influence of physical factors on spherulitic structures.[3] The building up of tension between slide and the thin polymer layer as a result of the difference in thermal expansivity is considered[4] to be a factor significantly affecting nucleation density.

According to some authors,[5,6] the crystallizing polymer may be considered to be a multicomponent system, some of whose components (mainly low molecular and stereoirregular constituents) are driven out of the crystallization sphere by growing crystals. It is indispensable for the further growth of crystalline formations that molecules capable of crystallization be in a position to diffuse to the surface of the growing crystals. This process is influenced by the viscosity of the medium and the temperature of crystallization. With decreasing viscosity of the medium and increasing crystallization temperature, formation of coarse spherulitic structure sets in.

According to our investigations, in contrast to the polymer mixtures, the small difference in morphology after treatment by method II and after conditioning under otherwise similar conditions indicates that the formation of larger crystalline structures (spherulites) is determined first of all by the viscosity of the mixture during crystallization. The decreased viscosity of the mixture during crystallization not only facilitates diffusion of molecules to crystallization centers but simultaneously facilitates also the segregation of two different polymers. With increased segregation of the polymers in the mixture, the influence of the amorphous component on crystallization of the crystalline component decreases.

It can be supposed that upon evaporation of solvent increased viscosity of the mixture can not be compensated even by temperature (within the temperature range in which supermolecular structures are emerging), and the mutual segregation of the components is impeded. Probably for this reason typical spherulites do not form, but only granulated structures. After brief heating of the mixture to temperatures considerably exceeding the melting point of the crystalline component (to 220°C.), no further formation of characteristic spherulites occurs during crystallization, regardless of the method of cooling. Spherulites formed in the sample when method I is used disappear after brief heating, and granulated morphological structures appear. A possible explanation of this phenomenon in a mixture of two polymers could be the increase of interpenetration of both components of the mixture, accompanied by an increase of contacting surfaces. It is interesting that the method of preparation of dis-

tinguishable spherulites proposed for crystalline homopolymers[7,2] also failed in crystallization of copolymers of polymethylene.[8] However, in contrast to polymer mixtures investigated by us, in copolymers previously formed spherulites were not destroyed. In a mixture of two polymers, in contrast to copolymers, the presence of the amorphous component may become more evident, especially at higher temperatures.

It should be emphasized that observation with a microscope having a separating power up to 0.85 μ was the only criterion of the interaction of the two polymers at different temperatures and viscosities. Thus observation of morphological changes of spherulites can be still considered, under the above conditions, as a conclusive change in the behavior of the components.

In accordance with the well known fact of the decrease in melting point on admixture of different substances and according to our own measurements there could be observed a lowering of the temperature intervals of mixtures (ΔT_m) in comparison with temperature intervals for the pure crystalline polymers. It might be supposed that even in the range of temperature intervals ΔT_c mutual miscibility of the components of the mixture occurs to some extent.

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Résumé

On a étudié la structure supermoléculaire de mélanges de polymères cristallins (polyéthylène de basse et haute pression, polypropylène isotactique) avec un polymère amorphe (polypropylène atactique) du point de vue de l'influence du composé amorphe sur la morphologie du composé cristallin. Des critères de changement de l'état morphologique des grandes formations supermoléculaires étaient constitués de l'image microscopique des échantillons obtenus avec un microscope optique à la fois avec des nicols croisés et avec contraste de phase. On a montré que la formation de sphérulites typiques dépend d'une part de la quantité de polymère amorphe ajouté d'autre part du traitement des échantillons. Par cristallisation en présence d'une faible quantité de solvant tel que le p-xylène, on observe la formation de sphérulites typiques du composant cristallin du mélange, alors que le même mélange dans le cas de l'évaporation du solvant présente une structure réfractive granulaire sans sphérulites typiques indépendamment de la vitesse de refroidissement. Le rôle probable du solvant consiste à faciliter la ségrégation mutuelle des microphases des deux polymères par suite d'une diminution de viscosité du mélange. On a en outre montré que même après un chauffage bref du mélange à température de 220°C, avant cristallisation, il n'y a pas formation de sphérulites; au contraire, les sphérulites originalement présentes disparaissent et une structure consistant en des formations réfractives et petites de polymères cristallins est formée. La formation

de cette structure visible après destruction de sphérulites peut être attribuée à une augmentation de l'interpénétration de deux polymères et à un accroissement des surfaces de contact entre les composants du mélange.

Zusammenfassung

Die übermolekulare Struktur von Mischungen kristalliner Polymerer (Niederdruck- und Hochdruckpolyäthylen, isotaktisches Polypropylen) mit einem amorphen Polymeren (ataktisches Polypropylen) wurde vom Gesichtspunkt des Einflusses der amorphen Komponente auf die Morphologie der kristallinen Komponente aus untersucht. Als Kriterium für die Änderung des morphologischen Zustands grösserer, übermolekularer Gebilde wurde das mit einem optischen Mikroskop zwischen gekreuzten Nicols und im Phasenkontrast erhaltene Bild der Probe verwendet. Es wurde gezeigt, dass die Bildung typischer Sphärolithe einerseits von der Menge des zugemischten amorphen Polymeren und andrerseits von der Behandlung der Proben abhängt. Bei Kristallisation in Gegenwart einer kleinen Menge Lösungsmittel (p-Xylol) kann die Bildung typischer Sphärolithe der kristallinen Komponente der Mischung beobachtet werden, während die gleiche Mischung im Falle der Verdampfung des Lösungsmittels, unabhängig von der Abkühlungsgeschwindigkeit, eine körnige, refraktive Struktur zeigt. Wahrscheinlich besteht die Rolle des Lösungsmittels in einer Erleichterung der wechselweisen Absonderung der Mikrophasen beider Polymeren durch Herabsetzung der Viskosität der Mischung. Weiters wurde gezeigt, dass auch nach kurzer Erhitzung der Mischung auf eine Temperatur von 220°C vor der Kristallisation keine Sphärolithe gebildet werden; es verschwinden, im Gegenteil, ursprünglich vorhandene Sphärolithe und eine aus kleineren, refraktiven Gebilden des kristallinen Polymeren bestehende Struktur wird erhalten. Die Bildung dieser nach der Sphärolithzerstörung auftretenden Struktur könnte auf eine stärkere gegenseitige Durchdringung beider Polymeren und eine Vergrösserung der Kontaktflächen zwischen den Mischungskomponenten zurückzuführen sein.