Colloid Polym Sci 275:520–529 (1997)
© Steinkopff Verlag 1997

ORIGINAL CONTRIBUTION

L. Minkova
Ts. Miteva
P.L. Magagnini

Crystallization behavior and morphology of PE-g-LCP copolymers

Received: 9 October 1996
Accepted: 13 January 1997

Dr. L. Minkova (✉) · Ts. Miteva
Institute of Polymers
Bulgarian Academy of Science
1113 Sofia, Bulgaria

P.L. Magagnini
Dipartimento di Ingegneria Chimica
University di Pisa
56126 Pisa, Italy

Abstract This study presents DSC and optical microscopy investigations on copolymers of semiflexible liquid crystalline polymer SBH 112 grafted to functionalized low molecular mass polyethylene (PEox) obtained by melt polycondensation or reactive blending procedures. The crystallization behavior of the PE-g-SBH copolymers has been studied under non-isothermal measurement conditions carried out at different cooling rates. The crystallization temperature (T_{cr}) of the PE component of the copolymers decreases steadily upon increasing the concentration of the SBH grafts. It was found that the copolymers prepared by reactive blending crystallize at slightly higher T_{cr} than those prepared by polycondensation and with a higher rate, confirmed by the determination of the crystallization rate coefficients (CRC). The results have been interpreted by the fact that the PE crystallizable segments and SBH grafts of the copolymers obtained by reactive blending are longer than those of the copolymers prepared by polycondensation. The overall nonisothermal crystallization kinetics has been studied by the Harnisch and Muschik equation. The results show that the mechanism of the crystallization of the PE phase changes only when the SBH content overruns ca.50%, due to the decrease of both nucleation and crystal growth rates.

The morphology of the copolymers crystallized nonisothermally from melt has been examined by polarization microscopy. Fairly homogeneous morphology with tiny PE spherulites is observed for PE-g-SBH copolymers prepared by polycondensation with SBH as the minor phase. No sign of the dispersed LCP domains can be recognized. On the contrary, the morphology of the copolymers prepared by reactive blending is distinctly biphasic. The allegedly longer PE segments crystallize into tiny spherulites too, but the LC domains formed by the long SBH branches present in this type of copolymers appear clearly in the micrographs at room temperature.

It is concluded that the copolymers prepared by reactive blending would be more effective as compatibilizers for PE/SBH blends than those prepared by polycondensation.

Key words PE-g-LCP copolymers – non-isothermal crystallization – crystallization kinetics – morphology

Introduction

It is well known that the addition of appropriate compatibilizers may help solving the problems of poor dispersion and poor adhesion in blends of incompatible polymers [1]. Among compatibilizing agents, block or graft copolymers made up of segments with chemical structure and solubility parameters that are identical or similar to those of the polymers being blended appear best suited to the scope [1, 2]. The compatibilization activity of the copolymers depend preferentially on the miscibility between the copolymer segments and the corresponding blend component, the copolymer structural and molecular weight characteristics, and the copolymer location on the blend interfaces [2]. Therefore, we undertook a research aimed at grafting a liquid crystal polymer onto functionalized polyethylene (PE-g-LCP copolymer) to be used as compatibilizer for PE/LCP blends. In previous papers [3, 4] two main procedures for preparing a PE-g-LCP copolymer have been described. According to the first procedure a successful synthesis of a PE-g-LCP by the polycondensation of the LCP monomers carried out in the presence of a PE sample containing free carboxylic groups (PEox) has been realized [3]. The second procedure involves a reactive blending of PEox with preformed LCP [4]. The copolymers formed were proved and investigated by IR spectroscopy, solid state NMR, DSC, thermogravimetry and SEM. It was shown that during the first procedure a fairly quantitative reaction of the carboxyl groups of PEox takes place, while only a part of PEox carboxyl groups undergo the transesterification during the second procedure [3, 4]. This leads to different structures of the copolymers obtained by both methods, namely different length of PE segments and LCP grafts. WAXS study of these copolymers has shown [5] absence of interactions in the crystalline phase or that of cocrystallization phenomena between the components of the copolymers. But both copolymer components are partly miscible in the amorphous phase and the extent of miscibility depends on the copolymer structure. The compatibilizing ability of the products with respect to HDPE/LCP blends has also been preliminarily demonstrated by SEM [3, 4].

It is well known that the properties of the crystalline polymer blends depend on their morphology which in turn is determined by the crystallization behavior of the blend components. In the case when a copolymer is added as compatibilizer the crystallization behavior of the system becomes more complicated. In the context of the miscibility between the crystallizable copolymer segments and the corresponding blend components it is important to study the influence of the grafts of the copolymer on the crystallization and morphology of the backbone and vice versa.

The valuable properties of block and graft copolymers, containing crystalline components, come from their ability to undergo microphase separation [6, 7]. The characteristics of the phase transitions in these systems depend on a number of factors affecting microphase separation and, accordingly, the structure, size and shape of the microphases. There is no simple relation between the crystallization characteristics of the copolymer components and their molecular structure parameters. But, it is well known that in the block or graft copolymers the transition temperatures and enthalpies of the crystallizable polymer segments decrease in comparison to those of the corresponding homopolymer [8]. The nucleation and crystal growth of the corresponding phases can be impeded since the components of the copolymers are covalently bonded. A similar behavior was observed by Tang et al. for PPMA-g-PEO copolymers [9], by Data et al. for EP-g-iPP copolymers [10] and by Jannasch et al. for PS-g-PEO copolymers [11].

In this work, the crystallization kinetics of PE-g-LCP copolymers obtained by polycondensation or reactive blending has been investigated under nonisothermal conditions and the results have been discussed with reference to the copolymers morphology. The processing of polymer blends proceeds usually under nonisothermal conditions. Moreover, the isothermal methods are often restricted to narrow temperature ranges and that is why the nonisothermal experiments may mean a great deal in view of the understanding of the crystallization behavior of such complicated systems as copolymers.

Experimental

The functionalized PE (PEox) sample, acid number of 28 mg KOH/g and a molar mass of ca. 10000 (ca. 5 carboxylic groups per mol), was supplied by Aldrich. The LCP was a laboratory sample of SBH 112 (Sebacic acid-S; 4,4′-dihydroxybiphenyl-B; 4-hydroxybenzoic acid-H) kindly provided by Eniricerche SpA, Milan. This semiflexible LCP has a crystalline to nematic phase transition temperature of 230 °C and a nematic to crystalline phase transition temperature of 217 °C [12].

The transesterification products – copolymers of SBH grafted on PEox were obtained by two main procedures [3, 4]. According to the first procedure the SBH synthesis is carried out in the presence of PEox which carboxyl groups are capable of entering the polycondensation reaction [3]. The product obtained consists chiefly of PE-g-SBH copolymer (COP) with a wide range of component content and of negligible amount of unreacted PEox. The second procedure consists of the catalyzed transesterification reaction between PEox and preformed SBH carried

Table 1 Composition of the investigated samples

Sample	Sample code	SBH content, [wt%]
Functionalized polyethylene	PEox	0
Mechanical blend PEox/SBH 50/50	MIX	50
PE-g-SBH copolymer 50/50, prepared by polycondensation	COP	50
– soluble in toluene	NCC	20
– soluble in xylene	SXC	30
– insoluble in xylene	RXC	75
PE-g-SBH copolymer 50/50, prepared by reactive blending for 120 min	COP120	50
– soluble in toluene	NCC120	0–5*
– soluble in xylene	SXC120	27
– insoluble in xylene	RXC120	73

* The SBH content in this fraction is not precisely determined due to the low SBH concentration (error ± 5% by thermogravimetry).

out in a Brabender mixer for 120 min mixing time. This procedure (reactive blending) leads to product COP120 containing appreciable amounts of unreacted PEox together with the formed copolymer PE-g-SBH [4]. For comparison, a physical blend of PEox and SBH in the same 50/50 w/w ratio (MIX) was prepared in the Brabender mixer without catalyst for mixing time 6 min. All the above products were successively fractionated with boiling toluene and xylene – good solvents for PEox and PE-g-SBH copolymers with low SBH content. The composition of the soluble fractions and the residues, determined thermogravimetrically [3, 4] is summarized in Table 1.

Calorimetric measurements were made with a Perkin Elmer DSC-7 equipment, calibrated with indium and tin standards, under an argon atmosphere. The specimens were heated to 190 °C and held at this temperature for 5 min in order to destroy the PE crystal nuclei. The DSC cooling traces were recorded with the rates of 2.5, 5, 10 and 20 °C/min. It must be pointed out that during the whole thermal treatment the LCP component in the PE-g-SBH copolymers remains in the crystalline state. The degree of crystallinity was calculated from the PE crystallization enthalpy normalized to the PE content. The crystallization enthalpy of 100% crystalline PE was taken as 293.1 J/g. The crystallization rate coefficient (CRC) was determined by the method proposed by Khanna [13]. For an accurate determination of the nonisothermal kinetic characteristics, the apparatus was calibrated at various scanning rates. The thermal lag between sample and pan holder temperatures was estimated according to the procedure of Eder and Wlochowicz [14]. The equation of Harnisch and Muschik was used for the determination of the Avrami exponents [15].

Optical microscopic observations were made on a Reichert Zetopan polarizing microscope equipped with a hot stage. In order to obtain thin films the powder-like specimens (COP and COP120 fractions) were heated to 260 °C, held at this temperature for 5 min and cooled down to room temperature with a rate of 10 °C/min. The photomicrographs were taken at room temperature. The Hv diffraction patterns of low-angle light scattering were obtained by applying the Bertran lens and using the microscope in the diffraction mode.

Results and discussion

Crystallization of PE-g-LCP copolymers

The crystallization of PE-g-LCP copolymers obtained by both procedures, i.e. polycondensation and reactive blending, have been investigated under nonisothermal

Table 2 Calorimetric data of the samples

Sample	2.5 °C/min		5 °C/min		10 °C/min		20 °C/min		α	CRC [1/h]	n
	T_{cr} [°C]	ΔH_{cr} [J/g]	T_{cr} [°C]	ΔH_{cr} [J/g]	T_{cr} [°C]	ΔH_{cr} [J/g]	T_{cr} [°C]	ΔH_{cr} [J/g]			
PEox	118.8	218.4	116.3	218.8	115.2	212.9	101.7	220.9	0.74	100	3.4
MIX	119.9	114.9	118.1	104.7	115.1	103.3	104.0	103.7	0.73	95	3.3
COP	112.7	94.7	110.5	90.2	106.5	94.9	94.6	90.6	0.63	73	3.3
NCC	114.0	178.7	112.1	177.2	108.0	171.1	98.5	181.1	0.75	75	3.3
SXC	112.2	128.6	110.2	123.0	107.3	128.3	100.7	127.5	0.68	73	3.0
RXC	110.4	22.3	108.5	20.6	102.8	20.4	95.3	21.0	0.30	60	1.6
COP120	114.8	82.1	113.0	95.6	109.4	91.2	103.3	96.4	0.65	83	3.4
NCC120	115.5	208.3	113.5	198.0	111.1	196.4	100.1	198.8	0.72	100	3.4
SXC120	114.0	150.1	112.1	148.9	107.3	148.2			0.70	67	2.9
RXC120	109.4	34.6	107.8	38.8	103.3	44.3	100.0	49.9	0.53	73	1.5

conditions using different cooling rates. The results of the measurements are collected in Table 2. The data on neat PEox and a mechanical blend of PEox/SBH 50/50 w/w (MIX) are also included for comparison.

The dependences of the crystallization temperature (T_{cr}) of the PE component on the SBH component concentration in COP and COP120 are shown on Figs. 1a and b. The corresponding values for the MIX are marked as single white points for comparison. It is apparent that at every cooling rate the crystallization temperature of PE component of the copolymers decreases steadily upon increasing the SBH component concentration, as could be expected for graft or block copolymers. It should be noted that the sample COP120 with 50 wt% SBH contains not only PE-g-SBH copolymers but some unreacted PEox [4]. That is why this sample crystallizes at T_c slightly higher (Fig. 1b) than it could be expected for PE-g-SBH copolymer containing 50 wt% SBH grafts. On the contrary, the crystallization temperature of PE component of the mechanical blend MIX, in which PE is not chemically bonded to the LCP, almost coincides with that of neat PEox at every cooling rate. The dependences of T_{cr} of the PE component on the SBH content are slightly different for COP and COP120, due to the different structure of PE-g-SBH copolymers, obtained by both methods. It is obvious that the copolymers of COP120 crystallize at temperatures slightly higher than those of COP, at equal content of SBH branches. This results could be explained by the higher length of the PE segments in the COP120 copolymers, because not all carboxylic groups of PEox enter transesterification during the reactive blending procedure [4]. It should be noted that the disturbance of PE component crystallization of the copolymers tends to fade at high cooling rate.

The crystallinity of the PE component (Table 2) of the mechanical blend MIX coincides with that of neat PEox (73%). PE component of the copolymers with SBH content lower than 50 wt% almost reaches the degree of crystallinity of the neat PEox too. The crystallinity of the PE component of the copolymers with 50 wt% SBH (COP, COP120) is lower (63%). The crystallinity of the copolymers with SBH content higher than 50 wt% decreases strongly in comparison to that of neat PEox. It should be pointed out that the PE component in RXC120 has a crystallinity higher than that in RXC and this could be explained by the longer PE segments in RXC120.

If the cooling rate is plotted against the crystallization temperature, the slopes of the straight lines drawn through the experimental points, according to Khanna [13], can be taken as the crystallization rate coefficients (CRC). As seen from the plots for COP and COP120 and their fractions in Figs. 2a and b, and from the CRC values (error ±3%) shown in Table 2, the CRC of the PE component of the

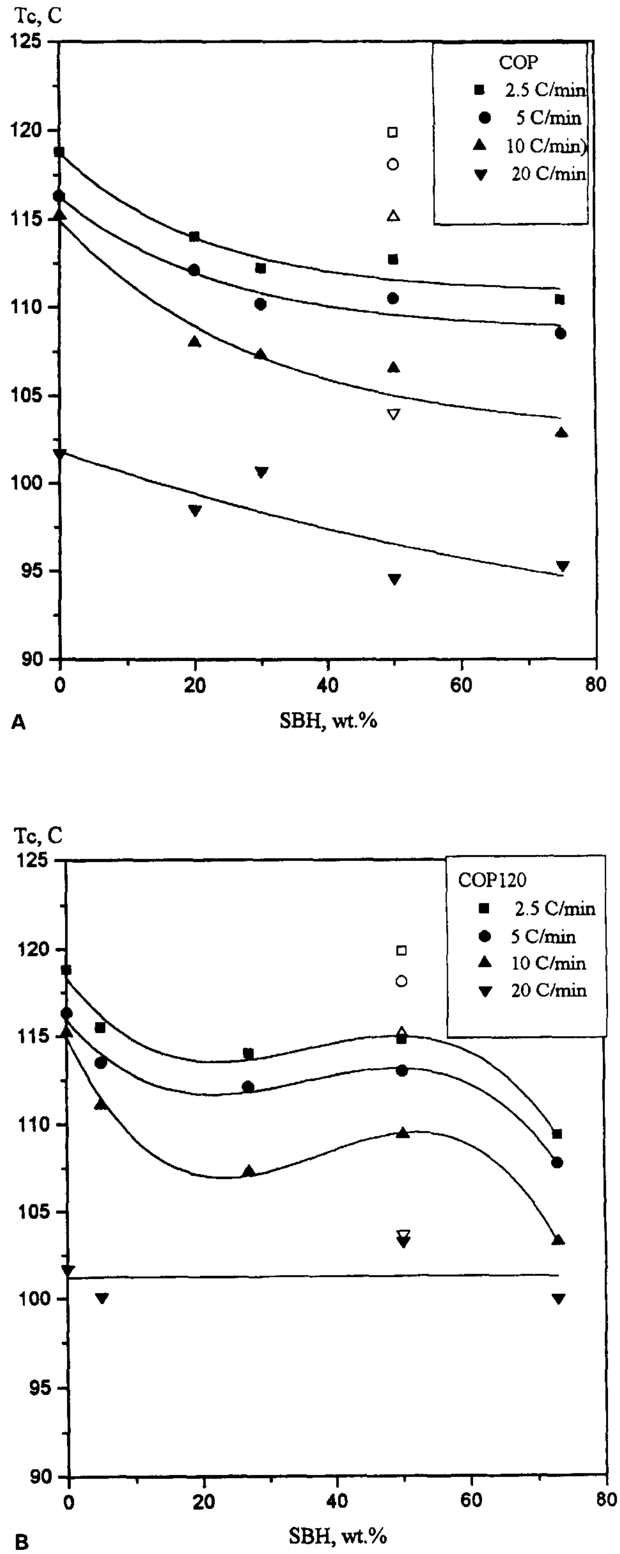


Fig. 1 Dependences of the crystallization temperatures (T_{cr}) of the PE component on the SBH component concentration in COP (**A**) and COP120 (**B**). The corresponding values for MIX are marked as single white points

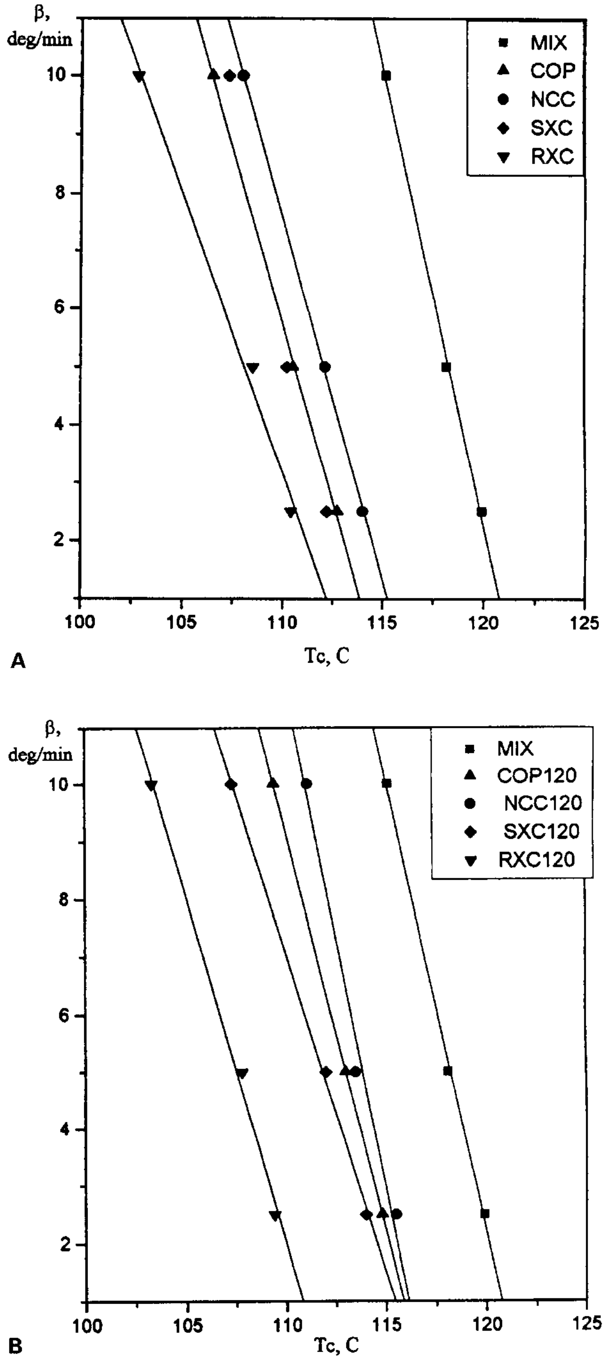


Fig. 2 Dependence of the cooling rate on the crystallization temperature of the samples: **A** COP and its fractions; **B** COP120 and its fractions

MIX (95 1/h) corresponds to the value found by Khanna for HDPE (98 1/h). For copolymers COP and COP120 with 50 wt% of SBH segments content the CRC values decrease to 73–83 1/h, and the CRC of COP120 copolymers are higher than those of COP copolymers. CRC value of NCC120 is very close to that of the PE component in the MIX, and this could be explained by low SBH segments concentration in this fraction. For copolymers with SBH content higher than 50 wt% the CRC value is 60 1/h for RXC, while that for RXC120 is 75 1/h. RXC and RXC120 copolymers are constructed from PE backbones with long SBH branches, but the PE segments of RXC120 are longer than those of RXC. This leads to easier crystallization of the PE segments of RXC120 and to CRC values higher than those of RXC.

The results show that under nonisothermal conditions the crystallization rate of the PE component of the PE-g-SBH copolymers is lower than that of the PE component of the mechanical blend MIX. The decrease of the crystallization rate depends on the concentration of the SBH component in the copolymers and on the copolymer structure. The decrease of the crystallization rate of copolymers is possible when an exclusion of the second component from the crystallizing phase during the crystallization process takes place. In fact, WAXS investigations have shown [5] that the SBH segments of the copolymers COP and COP120 do not enter the PE crystalline lattice. This means that during the PE crystallization the molten phase has been enriched in SBH component remaining in a crystalline state. These data confirm that the copolymers obtained during the reactive blending procedure crystallize at slightly higher rates than those obtained during polycondensation.

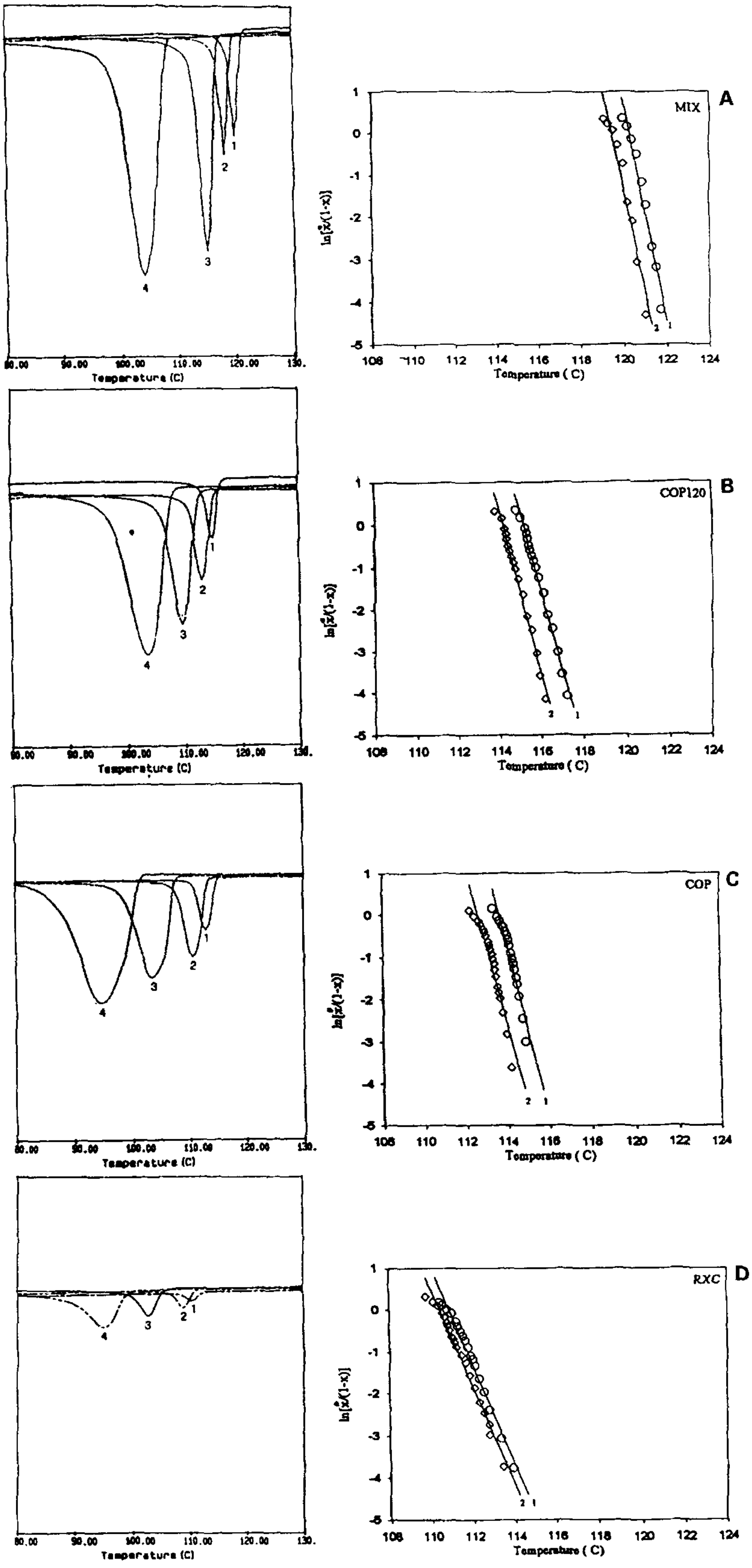
In order to receive information about the mechanism of the copolymers crystallization, the overall nonisothermal crystallization kinetics of the samples has been studied by the method of Harnisch and Muschik [15]. This method is based on the well-known Avrami theory for isothermal crystallization and gives the following equation for the determination of the Avrami exponent n:

$$n = 1 + (\ln(\dot{x}_1/1 - x_1) - \ln(\dot{x}_2/1 - x_2))/\ln(\beta_2/\beta_1)$$

at $T = T_c$ where $x_i(T)$ is the crystalline fraction calculated by integrating the DSC exotherma, $\dot{x}_i(T)$ is the derivative of x, representing the dH/dT value of the exothermic curve; β_i is the cooling rate. The Avrami exponent n depends on the type of nucleation and on the crystal growth geometry. At a certain cooling rate each thermogram supplies a pair of values $x_i(T_c)$ and $\dot{x}_i(T_c)$ for the chosen temperature T_c. The method requires the upper limit of the chosen T_c to be the T_{reaction} maximum, at which the fraction of the transformed material does not exceed 60%.

The Avrami exponents of the mechanical blend MIX, and of the copolymers COP and COP120 were determined by the plots of the values $\ln(\dot{x}_i/1 - x_i)$ versus T for the slower cooling rates 2.5 and 5 °C/min. The thermograms obtained at 20 °C/min cannot be used for the determination of n of the samples. In Fig. 3 the DSC thermograms of

Fig. 3 DSC thermograms of MIX (**A**), COP (**B**), COP120 (**C**) and RXC (**D**) and the corresponding Harnisch plots. Curve 1 – 2.5 °C/min cooling rate; curve 2 – 5 °C/min cooling rate; curve 3 – 10 °C/min cooling rate; curve 4 – 20 °C/min cooling rate



MIX, COP, COP120 and RXC, and the corresponding Harnisch plots are shown. Four types of samples are presented in Fig. 3: a mechanical blend MIX, in which the PE component does not change its crystallization rate in comparison to that of neat PEox (*a*, *a*′); PE-g-SBH copolymer (COP120), in which the PE crystallization rate is slightly decreased in comparison to that of neat PEox (*b*, *b*′); PE-g-SBH copolymer (COP), in which a strong retardation of the PE crystallization is observed (*c*, *c*′) and PE-g-SBH copolymer (RXC) with higher SBH content, characterized by lowest PE crystallization rate (*d*, *d*′). It is worth noting that the PE peaks for the mechanical blend MIX are sharper than the peaks of PE-g-SBH copolymers in COP120 and especially than those of COP. Moreover, the Harnisch plots of the investigated copolymers appear as straight lines until the upper limit of T_c, at which the fraction of the transformed material is about 30%.

Values of $n = 3.3$–3.4 were obtained for the PE component of MIX, COP120, COP and their fractions NCC120 and NCC, which are characteristic for heterogeneous nucleation followed by spherulitic tridimensional growth. The change of $n (n = 3)$ is not very significant for the copolymers SXC120 and SXC, with the content of SBH graft segments lower than 50 wt%. For copolymers with the content of SBH graft segment higher than 50 wt% (RXC120 and RXC) the values of $n = 1.5$–1.6 were obtained, which is characteristic for heterogeneous nucleation and monodimensional crystal growth. It should be pointed out that the above values of the Avrami exponents were determined for the first stages of the PE crystallization, at which the fractions of the transformed material do not exceed 30%. During the last stages of crystallization and the secondary crystallization the values of n drop to 1–1.5. At fractions of the transformed material exceeding 30% the effect of impingement and truncation of spherulites become very important. If an impingement and truncation occur, the overall rate of crystallization decreases and the mechanism of crystallization may change. Ultimately, the value of the Avrami exponent decreases.

The obtained results show that the decrease of the PE crystallization rate for the copolymers with SBH content lower than 50 wt% does not lead to a change in the crystallization mechanism (i.e. the type of nucleation and the geometry of the crystal growth). For the copolymers with SBH content higher than 50 wt% the PE crystallization mechanism changes. This is due to the strong decrease of the overall crystallization rate of these copolymers, i.e. to the decrease of the nucleation rate and of the crystal growth rate. The decrease of the crystal growth rate of the copolymers in comparison to the corresponding homopolymers is a common finding explained by the lower mobility of the crystallizable segments of the copolymers [16]. The obtained values of $n = 1.5$–1.6 (monodimensional crystal growth) indicate that the crystal growth of these copolymers is controlled by diffusion.

Morphology of PE-g-SBH copolymers

For the NCC120 fraction, containing 5 wt% SBH, a mainly isotropic melt is observed at temperatures higher than the melting point of PE. After the crystallization big banded spherulites (Fig. 4a) are formed, similar to those observed for neat PEox under the same crystallization conditions. On the contrary, for the NCC fraction, containing 20 wt% SBH, small birefringent domains can be seen in the film at temperatures higher than the PE melting point. These domains do not aggregate even at temperatures higher than the SBH melting point. On cooling NCC crystallizes in spherulitic structures with dimensions several times smaller than those of the NCC120 spherulites, confirmed by typical spherulitic Hv diffractogram (Fig. 5a). It may be interesting to point out that the micrograph after crystallization of the latter fraction fails to show the presence of a dispersed phase. This can be explained assuming that SBH is contained in this fraction as fairly short branches chemically bonded to the PE chains and is therefore unable to segregate as a separate phase. In fact, the WAXS investigations of NCC showed [5] that the short SBH segments do not give rise to a crystalline phase, but enter the amorphous phase of the PE-g-SBH copolymer. It was shown [3, 4] that during the fabrication of COP almost quantitative esterification of PEox carboxylic groups is achieved, while during the fabrication of COP120 not all PEox carboxylic groups enter the transesterification reaction. This leads to PE segments in PE-g-SBH copolymers of COP shorter than those of COP120. So, the smaller PE spherulite dimensions in NCC in comparison to those in NCC120 could be explained by the lower PE crystal growth rate in NCC, resulting from the shorter crystallizable PE chains.

The results show that the morphology of the toluene soluble fractions of the copolymers NCC120 and NCC is a homogeneous one. PE spherulitic structures are mainly observed, whose dimensions depend on the different length of the PE chains in the NCC120 and NCC copolymers, crystallizing at different rates. The SBH graft chains of NCC120 and NCC copolymers being very short are unable to form a separate crystal phase so that they enter the amorphous phase of the copolymers. No cocrystallization is observed for both components, confirmed also by WAXS investigations.

When we melt the xylene soluble fractions SXC120 and SXC, containing ca. 30 wt% SBH, a lot of SBH birefringent domains can be seen at temperatures above the PE melting point. These domains do not aggregate even at

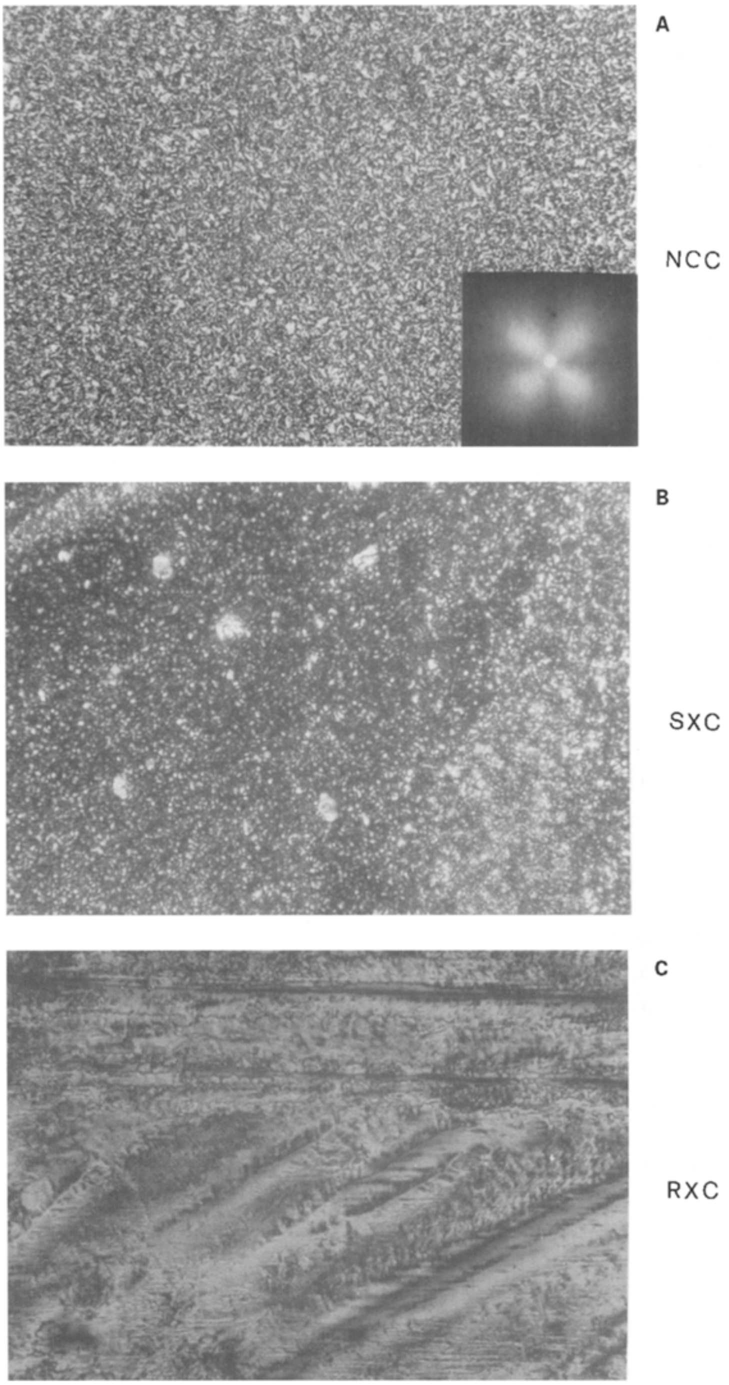


Fig. 4 Optical micrographs of COP fractions: **A** NCC; **B** SXC; **C** RXC

temperatures higher than the SBH melting point. On cooling, the two component segments crystallize in different crystal structures. The morphology of these fractions at room temperature is not homogeneous: small spherulitic structures and small birefringent liquid crystal domains can be seen (Figs. 4b and 5b). The two types of structures are very well dispersed and in some areas of the micrographs they are indistinguishable. The X-ray patterns also confirm that in SXC120 and SXC, the SBH segments give rise to a separate crystal phase [5]. This result could be explained by the fact that SBH chains in these copolymers are longer than those in toluene-soluble fractions. The PE component crystallizes in tiny spherulites due to the low crystal growth rate of PE segments in SXC120 and SXC

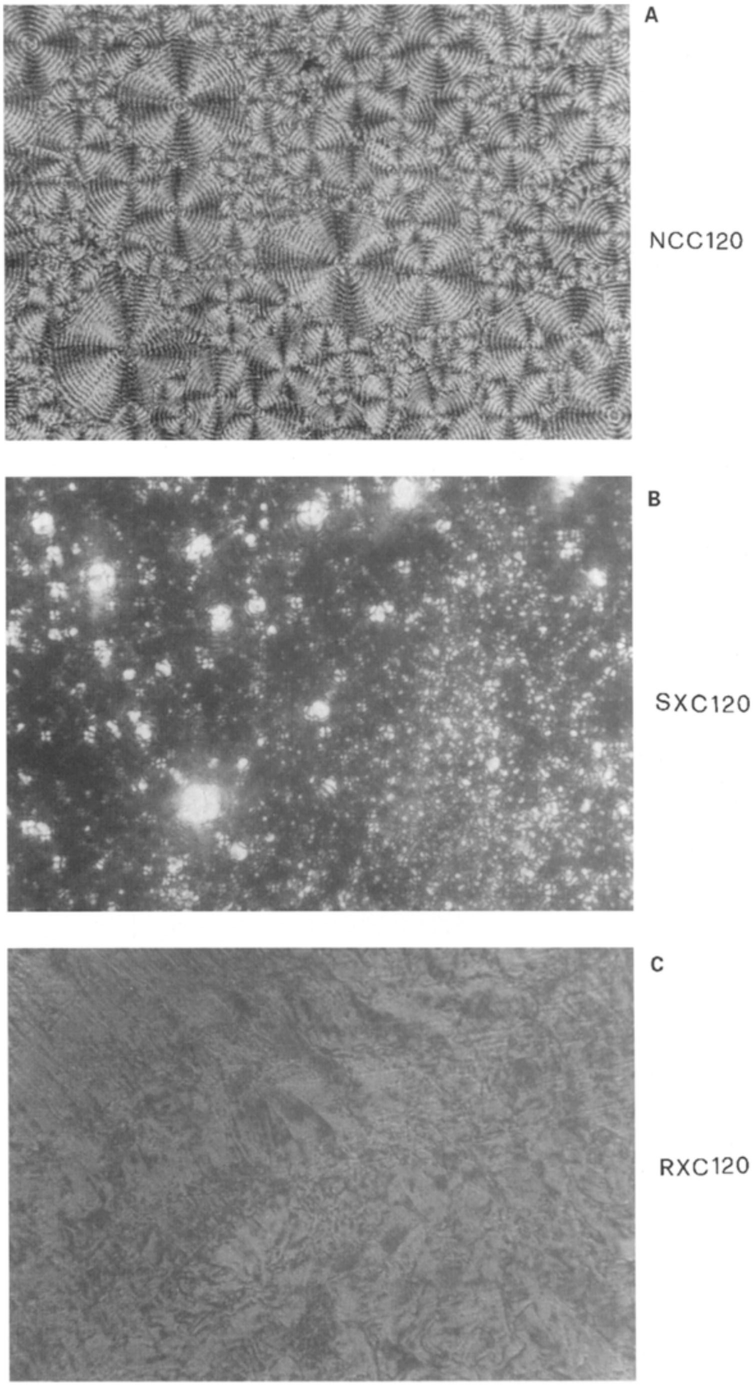


Fig. 5 Optical micrographs of COP120 fractions: **A** NCC120; **B** SXC120; **C** RXC120

copolymers determined by the low mobility of the PE chains bonded to long SBH grafts.

When we melt the insoluble fractions of the copolymers RXC120 and RXC, containing ca. 75 wt% SBH, thin films can be obtained only at temperatures higher than the SBH melting point. Large birefringent liquid-crystal domains are observed in RXC120 and RXC melts. The crystallization of the PE component of the fractions cannot be detected on cooling, and the SBH domains remain the same up to room temperature (Figs. 4c and 5c). Banded textures typical for a nematic LCP can also be seen on the micrographs taken at room temperature. This morphology confirms that the insoluble fractions contain SBH polymer and PE-g-SBH copolymer, in which the SBH component predominates. It was shown by WAXS study that the PE component of the copolymers crystallizes in a separate crystalline phase. Unfortunately, the morphology of the PE crystalline phase cannot be determined due to the very strong birefringence of the LCP domains. Taking into account the DSC determined mechanism of crystallization, it can be assumed that the PE chains in RXC120 and RXC crystallize in monodimensional nonspherulitic structures. This is due to the very low mobility of the PE chains bonded to very long SBH graft chains.

Conclusion

The crystallization behavior and the morphology of PE-g-SBH copolymers, obtained by reactive blending or polycondensation, depend on the copolymer structure namely on the length of PE segments and SBH grafts. The copolymers obtained by reactive blending (COP120) are constructed of long PE backbones with SBH graft chains relatively longer than those of the copolymers prepared by polycondensation (COP); the crystallizable PE segments are also longer than those in COP. PE chains of the copolymers prepared by reactive blending crystallize at higher T_{cr} and with higher rate than those of the copolymers prepared by polycondensation; moreover, the crystallization mechanism of the PE phase changes only when the SBH content increases beyond ca. 50%. The morphology of these copolymers (COP120) is distinctly biphasic. The allegedly longer PE segments crystallize in tiny spherulites and the LC domains formed by long SBH branches present in this type of copolymers do appear clearly in the micrographs at room temperature.

The results show that the crystallization behavior and morphology of the copolymers obtained by reactive blending (COP120) are more similar to those of the neat components of PE and SBH. Hence, these copolymers would be most effective for a compatibilizer for PE/SBH blends than the copolymers prepared by polycondensation (COP).

Acknowledgments This work was carried out within the framework of Copernicus Program (Contract n. CIPA-CT94-0118) funded by the Commission of the European Communities.

References

1. Folkes MJ, Hope PS (1993) Polymer Blends and Alloys. Blackie Academic & Professional, London
2. Lyatskaya Y, Gersappe D, Gross N, Balazs A (1996) J Phys Chem 100:1449
3. Magagnini PL, Paci M, Minkova LI, Miteva Ts, Sek D, Grobelny J, Kaczmarczyk B (1996) J Appl Polym Sci 60:1665
4. Minkova LI, Miteva Ts, Sek D, Kaczmarczyk B, Magagnini PL, Paci M, La Mantia FP, Scaffaro R, J Appl Polym Sci, in press
5. Miteva Ts, Minkova L, Colloid & Polymer Sci, in press
6. Manson JA, Sperling LH (1976) Polymer Blends and Composites. Plenum Press, New York
7. Noshay A, McGrath JE (1977) Block Copolymers–Overview and Critical Survey. Academic Press, New York
8. Mathot Vincent BF (1994) Calorimetry and Thermal Analysis of Polymers. Hanser Publishers, Munich
9. Tang T, Huang B (1994) J Polym Sci B 32:1991
10. Datta S, Lohse D (1993) Macromolecules 26:2064
11. Jannasch P, Wesslen B (1995) J Polym Sci A33:1465
12. Pedretti U, Roggero A, Citta V, Montani E, La Mantia FP, Magagnini PL (ed) (1993) Processing and Properties of Liquid Crystalline Polymers and LCP Based Blends. Chem Tec Publishing, Canada
13. Khanna YP (1990) Polym Eng Sci 30:1615
14. Eder M, Wlochowicz A (1983) Polymer 24:1593
15. Harnisch K, Muschik R (1983) Colloid & Polymer Science 261:908
16. Wunderlich B (1979) Macromolecular Physics, Vol 2. Mir, Moscow, p 344