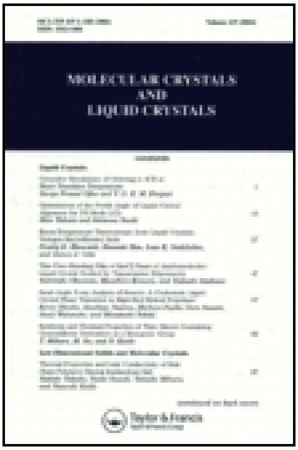

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Molecular Order, Phase Transitions and Chain Mobility in Liquid Crystalline Copolyesters

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MOLECULAR ORDER, PHASE TRANSITIONS AND CHAIN MOBILITY IN LIQUID CRYSTALLINE COPOLYESTERS

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Abstract. Poly(ethylene naphthalene-2,6-dicarboxylate) (PEN) and copolyesters of PEN and p-hydroxybenzoic acid (PHB) containing different amounts of PHB ranging from 10 to 90 mole-% were synthesized and studied by wide angle X-ray scattering employing synchrotron radiation, by DSC and microscopically. The copolyesters form liquid crystalline states if their content of PHB exceeds 30 %. In the materials containing up to 50 % PHB, crystals of PEN are formed, in those containing 80 and 90 % PHB, crystals of poly-PHB are found. The influence of the PHB content on the melting point and on the kinetics of crystallization is investigated.

In addition, copolyesters of poly(ethylene terephthalate) (PET) and different amounts of PHB were synthesized. By means of deuteron NMR it has been found, that the PHB groups decrease the mobility of the PET groups considerably. Small angle neutron scattering experiments show that in the liquid crystalline state, the molecules are far away from being extended.

INTRODUCTION

A great variety of liquid crystalline main chain polymers are statistical copolymers consisting of rigid units (mesogenic groups) and flexible units, both of which are able to crystallize. If the fraction of the rigid units is increased, the chains become less flexible. When a critical fraction is reached, the material is enabled to form liquid crystalline states.

For such copolymers several questions arise:

1. Which is the minimum fraction of rigid units that must be present in order to form liquid crystalline states?
2. Which of the two components crystallizes in copolymers of different compositions?
3. How does the composition influence the transition temperatures (glass transition, melting point, nematic-isotropic), the chain mobility and the rate of crystallization?
4. How completely are the molecules extended in the nematic state?

In order to investigate these questions, copolyesters of poly(ethylene naphthalene-2,6-dicarboxylate) (PEN) and p-hydroxybenzoic acid (PHB) have been synthesized by transesterification of PEN with p-acetoxybenzoic acid1). The composition of the copolyesters has been changed in steps of 10 mole-%, thus obtaining copolyesters with a content of 90, 80, ... , 20, 10 mole-% of PEN.

The crystallization behavior of the homopolymers PEN and of poly(4-hydroxybenzoate) (poly-PHB) was investigated earlier1,2,3). PEN can be obtained in the amorphous glassy state by quenching from the melt in ice water. The glass transition temperature is 120 °C. By annealing at temperatures below 200 °C PEN crystallizes in the so called α-modification. Above 200 °C the β-modification is obtained. After it is formed, each crystal modification is stable up to its melting point at 270 °C. Poly-PHB, the other component of the copolyester, is always crystalline. At 330 °C, it shows a reversible transition from a low temperature modification with several crystal reflections into a high temperature modification with one main reflection2,3).

As it was difficult to obtain deuterated PEN, the investigations of the chain mobility by deuteron NMR and the studies of the conformations of the chains by neutron scattering were performed on copolyesters of poly(ethylene terephthalate) (PET) and PHB. The copolyesters were obtained from PET and p-acetoxybenzoic acid by transesterification as described by Jackson and Kuhfuss4). The synthesis of deuterated PET and deuterated PHB is described elsewhere5,6). These copolyesters form liquid crystalline states if the amount of PET is 60 mole-% or less7,8).

Wide angle X-ray scattering (WAXS) measurements were performed on a synchrotron radiation beamline$^{9)}$ at HASYLAB, DESY, Hamburg and on a conventional goniometer (Siemens D 500). For microscopic investigations a Leitz polarization microscope and a hot stage produced by Linkam were used. Calorimetric measurements were performed on a Perkin Elmer DSC IV. The neutron scattering was measured at the ILL in Grenoble. The deuteron NMR investigations were carried out on a Bruker MSL 300 spectrometer.

OCCURRENCE OF LIQUID CRYSTALLINE STATES

In order to find out whether the copolyesters with different compositions can form liquid crystalline states, a thin film (10 μm) of each composition was heated up in a microscope with crossed polarizers. The birefringence pattern obtained, was observed as a function of temperature. Pure PEN as well as the copolyesters containing 90 and 80 mole-% PEN were partially crystalline at room temperature and became an isotropic melt at 270 °C, 260 °C and 250 °C respectively. It was not possible to obtain them in a liquid crystalline state. In copolyesters containing 70 mole-% of PEN or less, birefringence patterns were observed above the melting point, proving that these materials had become liquid crystalline. At temperatures close to the melting point (region LC1 in Fig. 5) a fine grain texture is observed, at higher temperature (region LC2 in Fig. 5) a schlieren texture can be seen, corresponding to a nematic structure. The nature of the fine grain liquid crystalline texture is not yet clear. We first assumed that it might be a smectic phase. However, no corresponding X-ray diffraction reflection could be observed.

It is interesting to note that a liquid crystalline state can be formed if the amount of PHB is only 30 mole-%. In copolyesters of PET and PHB the amount of PHB has to be at least 60 mole-% in order to form liquid crystalline states. This difference may be due to the fact that the naphthalene ring in the PEN units contributes more to the stiffness of the molecules than the benzene ring in the PET units.

WHICH COMPONENT CRYSTALLIZES?

In order to investigate the ability of the two components of the copolyester to crystallize, 200 μm thick films were prepared by melt pressing and quenching in ice water. The wide angle X-ray scattering of each film was measured. Afterwards the films were annealed at 200 °C for 1 hour and the wide angle X-ray scattering was measured again. The scattering patterns obtained immediately after quenching are shown on the left hand side of Fig. 1, those measured after annealing can be seen on the right side of this figure. The fraction in mole-% of PEN is given as a parameter at each curve. Some of the samples were slightly oriented, probably due to flowing during the melting process. The scattering of these samples was measured on the meridian.

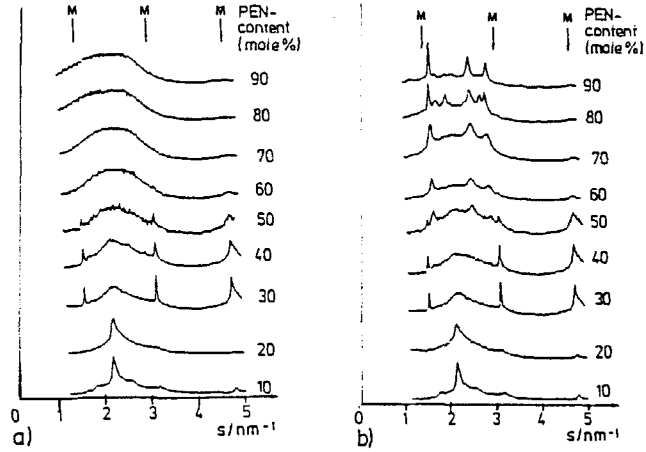

Fig. 1 WAXS of PEN/PHB copolyesters a) quenched b) annealed 1h at 200 °C. M indicates the position of the meridional reflection corresponding to the intramolecular interference as explained by Blackwell and Gutierrez[10)]

The scattering diagrams of the annealed materials containing 90, 70, 60 and 50 mole-% PEN show the crystal reflections of the α-modification of PEN. The diagram of the materials containing 80 mole-% PEN shows the reflections of the β-modification of PEN. The materials containing 20 and 10 mole-% PEN show the crystal reflections of the high temperature modification of poly-PHB at $s = 2.2\ \mathrm{nm}^{-1}$. However, the reflection is much broader than in the case of poly-PHB. The materials with 30 and

40 mole-% PEN show neither the PEN nor the poly-PHB reflections. With these and some other materials, additional reflections appear, both with the annealed and the quenched samples. Their positions are indicated by M in Fig. 1. These reflections are due to the alternation of different sequences in the copolyester, as it was shown for other liquid crystalline copolymers by Blackwell and Gutierrez10).

These results show that in the copolymer, PEN has a strong tendency to crystallize. Even if the amount of PEN is only 50 mole-%, crystals appear, though the amount of crystallized PEN as estimated from calorimetrical results and from X-ray diffraction is only about 10 %. On the other hand, the tendency of PHB to crystallize is much smaller. Only in molecules containing 80 and 90 mole-% PHB, crystals of this component appear. These crystals only exist in the more open structure of the high temperature modification. In addition, the half width of the reflection increases considerably with decreasing content of PHB. Obviously, in the copolyester, the crystals have a lower degree of order than in pure poly-PHB. These results show that the formation of poly-PHB crystals is much more hindered by the presence of 10 or 20 mole-% PEN than the formation of PEN crystals is hindered by the presence of 10 or 20 mole-% PHB.

PHASE TRANSITIONS

Fig. 2 shows some typical DSC diagrams. With the quenched materials, while raising the temperature, first a step or small peak is observed indicating the glass transition. This is followed by an exothermic peak due to crystallization. Finally an endothermic peak is observed, which is caused by melting. Materials annealed after quenching do not show a crystallization peak. Their melting is accompanied by two peaks, probably caused by superposition of melting and recrystallization.

Fig. 3a represents the temperature T_m at the end of the melting range and the temperature T_m' at which the second peak of the DSC curves appears as a function of the PEN content as measured with the annealed samples. Fig 3b shows the enthalpy of melting. The point at 0 mole-% PEN refers to the change of the crystal modification in PEN.

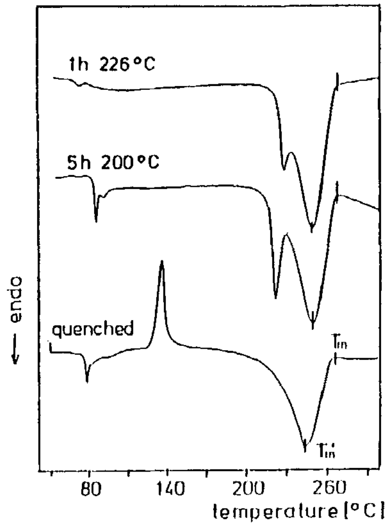

Fig. 2 DSC curves of PEN/PHB (60:40) after different heat treatment. Heating rate: $10^{0}C\ min^{-1}$

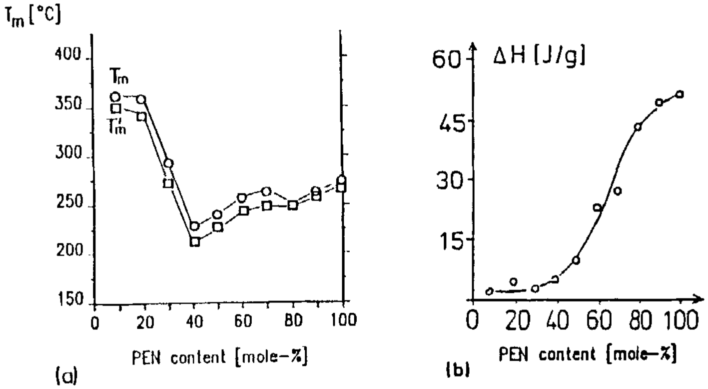

Fig. 3 Melting temperature T_m and enthalpy of melting H_m of PEN/PHB copolyesters as a function of the PEN content. ○ end of melting range (T_m), □ position of second peak of DSC curve (T_m').

According to the WAXS investigations, with the copolyesters containing 50 mole-% and more PEN, the DSC melting peak is accompanied by the disappearance of the

PEN crystal reflections. This proves that, within this range of compositions, the endothermic peak is caused by the melting of PEN. The melting point decreases with decreasing amount of PEN as a consequence of the entropy of mixing and of a decrease of crystal size. As an exception, the melting point increases when the PEN content changes from 80 to 70 mole-%. This must be attributed to the fact that, during melting, the material containing 80 mole-% PEN goes over into an isotropic melt while that containing 70 mole-% PEN goes over into a liquid crystalline phase, which has a smaller entropy than the isotropic melt. It has to be pointed out that a transition is also observed for materials containing less than 50 mole-% PEN. Their scattering diagrams show no PEN crystal reflections. In case of the copolyesters containing 20 and 10 mole-% of PEN, the DSC melting peak is accompanied by the disappearance of the crystal reflection of the high temperature modification poly-PHB (Fig. 4). This proves that, in these copolyesters, melting of poly-PHB is observed. This is worthwhile noting because with the homopolymer of PHB no melting can be observed before degradation takes place. In the copolyester containing 30 and 40 mole-% of PEN, the DSC peak is probably caused by melting of PHB crystals which are too small to show reflections in a WAXS diagram.

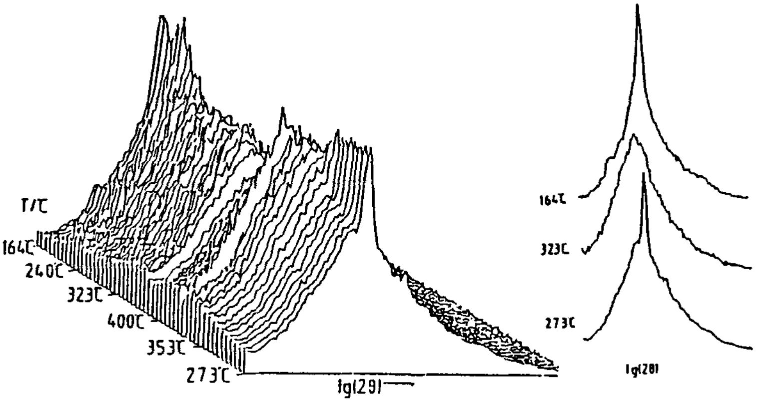

Fig. 4 Change of WAXS of PEN/PHB (20:80) during heating and cooling.

The phase diagram in Fig. 5 shows the glass transition temperatures, the melting points and the regions in which the different crystals are formed. The regions in which the liquid crystalline fine grain structure and the liquid crystalline schlieren texture appear are also shown and indicated by LC1 and LC2 respectively. In addition, the clearing point was determined by a polarization microscope. The results are represented by the upper curve in Fig. 5, separating the range of liquid crystals from that of the isotropic melt. It must be pointed out however, that the transition from the liquid crystalline phase to the isotropic melt took place within a temperature range of about 30 °C. Within this range islands of isotropic melt appeared and increased in size and number. This is not a kinetic effect, because no increase of amount of isotropic melt could be observed if the sample was kept at constant temperature. We think that the broad transition range is due to chemical heterogeneities of the molecules. In Fig. 5, the temperature represented, is always that of the end of the transition.

The point on the abszissa at 330°C represents the temperature of transition of poly-PHB from the low temperature crystal modification (LTCM) to the high temperature crystal modification (HTCM). It is not yet known if the LTCM of poly-PHB can also be obtained in the copolyesters. Therefore only a hypothetical transition line between the LTCM and the HTCM is shown in the figure.

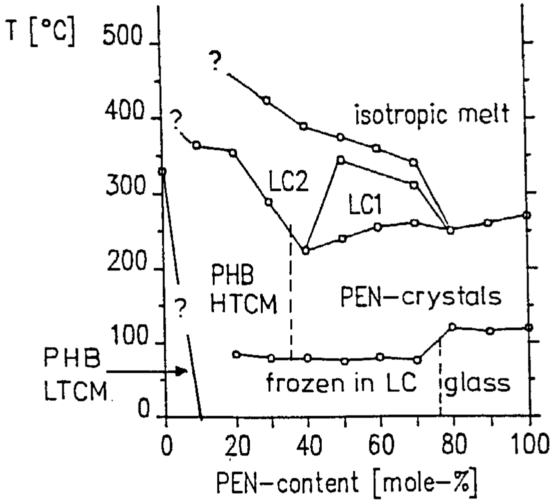

Fig. 5 Phase diagram of PEN/PHB copolyesters.

The dependence of the glass transition temperature T_g on the PEN content is unusual: T_g is constant (about 120°C) for PEN contents between 100 and 80 mole-% and it drops to another constant value (about 80°C) for PEN contents of 70 mole-% and less. The change occurs at the same temperature at which the copolyesters become able to form liquid crystalline states.

RATE OF CRYSTALLIZATION

The copolyesters containing different amounts of PEN were brought into a furnace which was inserted into the synchrotron beam. They were isothermally crystallized at different temperatures T_c after cooling quickly from 280°C to T_c or, at low temperatures, by heating up the amorphous samples from room temperature to T_c. The process of crystallization was followed by measuring WAXS.

Fig. 6 shows the half time of crystallization τ as a function of the crystallization temperature T_c. Fig. 7 shows the temperatures T_c^* and T_c^{**} at which the half time of crystallization is 4 min, as a function of the PEN content. In this figure, T_m and T_g are plotted too. At high temperatures, the samples with all compositions show a similar dependence of τ on T_c if the change of T_m with composition is taken into account. Thus, in Fig. 7, the curve representing T_c^{**} accurately follows that representing T_m. At low temperatures however, T_c^* decreases continuously with decreasing PEN content, while T_g first stays constant and, at a PEN content between 80 and 70 mole-%, drops down to another constant value. The distance between T_c^* and T_g considerably decreases with decreasing PEN content as long as the material is not able to form a liquid crystalline state. As a consequence, the material containing 80 mole-% PEN starts to crystallize 15°C above T_g, while pure PEN crystallizes only if it is heated at least 40°C above T_g. Obviously, the PHB units, without decreasing T_g, increase some sort of chain mobility which is sufficient for crystallization.

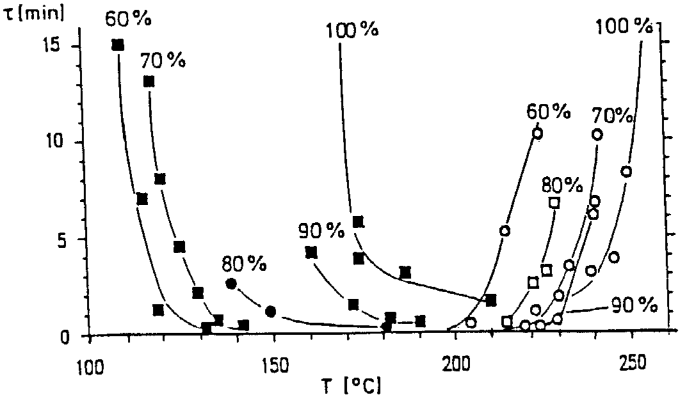

Fig. 6 Half time of crystallization τ as a function of crystallization temperature T_c of PEN/PHB after melting at 280 °C. The parameter is the PEN content. ■ α-modif. from glass, □ α-modif. from melt, ○ β-modif. from melt.

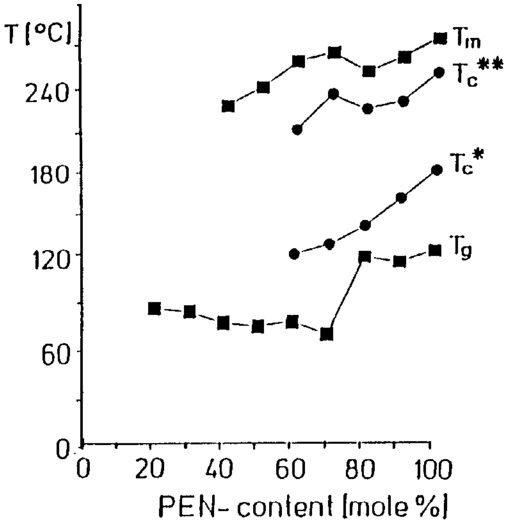

Fig. 7 Melting temperature T_m, glass transition temperature T_g and temperature of crystallization with half times of 4 min. T_c^* and T_c^{**} as a function of PEN content.

For the discussion of the crystallization from the frozen in liquid crystalline state, one has to consider the following: If PET is oriented before crystallization, the rate of crystallization is considerably increased[11,12]. Crystallization occurs at temperatures much closer to the glass transition than in the case of unoriented material. Obviously, the parallelization of the chains which occurs as a consequence of orientation enhances the process of crystallization. As the chains are well parallelized within the domains of nematic liquid crystalline polymers, one expects a similar increase in the rate of crystallization if one compares the crystallization of a nematic liquid crystalline material with that of an isotropic melt. As Fig. 7 shows, this is not the case. In contrast, the difference between T_c^* and T_g becomes larger when the material crystallizes from the liquid crystalline state. The reason for this might be the following one: In contrast to oriented PET, in the statistical copolyesters the chains must perform longitudinal diffusion before PEN units are neighboured by other PEN units and crystallization can take place. In addition the chain mobility is decreased considerably in the liquid crystalline phase as shown below (see section CHAIN MOBILITY).

CONFORMATIONS OF THE CHAINS

The radius of gyration of the chains in the frozen in liquid crystalline state of a copolyester PET/PHB containing 60 mole-% PET was determined by small angle neutron scattering investigations on a blend of deuterated and nondeuterated material, in a similar way as with pure PET[5,13,14]. The blends were prepared by coprecipitation from a solution in phenol-tetrachloroethane with ethanol. The powder obtained was meltpressed at 250 °C for 30 s and quenched. From a Zimm plot of the absolute neutron scattering intensities, a value of 0.058 nm was found for the ratio of the average radius of gyration and the square root of the molecular weight $(R^2_{gw}/M_w)^{1/2}$. The corresponding value for the homopolymer PET is 0.037 nm[5,13], which is in agreement with theoretical calculations for a random Gaussian chain. The larger value for the copolyester may be attributed partly to an increase of R^2_{gw} which the stiff PHB units cause in a Gaussian chain. Partly it must result from the fact that the polymer is in a nematic state. In any case, this result demonstrates that the increase of the radius of gyration occurring if the material is transformed from the isotropic into the nematic state is less than by a factor of two. Thus, in the nematic state, the molecules are far away from beeing completely extended. More detailed results are reported elsewhere[15].

CHAIN MOBILITY

Deuteron NMR is a new powerful tool for the investigation of molecular mobility[16]. Therefore, we have synthesized PET / PHB copolymers containing 80 and 60 mole-% PET respectively in which the benzene ring in the PET units was deuterated (bd_4). In addition a set of similar samples was synthesized in which the CH_2-groups were deuterated (ed_4). Fig. 8 shows the deuteron NMR spectra of these materials together with the spectrum of the partially deuterated homopolymer PET at 115 °C. For the PET with deuterated benzene rings (upper row in Fig. 8) a sharp line in the center of the spectrum is obtained, indicating that the benzene rings in the amorphous regions perform an isotropic motion[17]. The additional doublet arises from the rigid benzene rings within the crystals. In the copolyesters, no sharp central line is observed. From

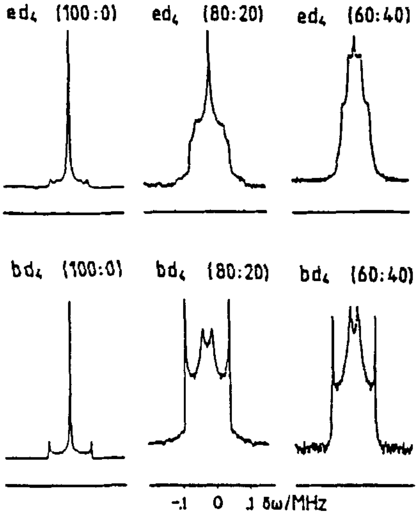

Fig. 8 Fully relaxed d NMR spectra of PET, PET/PHB (80:20), and PET/PHB (60:40) at 115°C. Above: ethylene groups are deuterated. Below: benzene rings in PET are deuterated.

this one has to conclude that, at 115^{o}C, the benzene rings in the copolyesters do not perform an isotropic motion though the glass transition temperature is as low as 70°C, exactly as with the homopolymer PET. Similar results are obtained with respect to the CH_2 groups.

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