Phase separation in a thermotropic copolyester via spinodal decomposition

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SUMMARY

Novel experimental evidence is presented for the phase heterogeneity of a thermotropic copolyester containing 50 % of p-hydroxybenzoic acid (HB). Characteristic phase morphologies accompanying spinodal decomposition in polymer blends can be detected. Fractionation and a NMR-analysis demonstrate that the copolyester contains two constituents which differ in their HB-contents.

INTRODUCTION

Recently, it has been interesting to introduce transition studies of copolymers with rigid chain molecules, which frequently display liquid crystallinity. One of the first thermotropic liquid crystalline polymers was obtained by a transesterification reaction of poly(ethylene terephthalate) (PET) and p-acetoxybenzoic acid in the melt phase by Jackson and Kuhfuss /1-3/. These copolyesters (coded P(ET-co-HB)) display liquid crystallinity at or above 40 mol% HB /4/. However, it has been shown that the copolyesters are often heterogeneous systems with at least a HB-rich and a ET-rich phase. The multiphase character has been demonstrated by studies of thermal properties /5,6/, dynamic mechanical measurements /7/, morphological studies /8/, X-ray diffraction measurements /9/ and fractionation investigations /10/. Furthermore, there is some experimental evidence that the chemical synthesis leads to copolymers which are not completely random but tend to multiblock systems /11/. This is supported by recent results of the sequence analysis based on NMR-studies /12,13/.

In this paper the phase heterogeneity of a copolyester is monitored by phase separation. Fractionation reveals two components comprising different HB-contents. NMR-studies allow more insight into their chemical nature.

EXPERIMENTAL

Materials: The P(ET-co-HB)-50/50 (mol%) was synthesized as usual /1-3/. The fractionation was made by refluxing the copolyester three times in a large excess of chloroform for 24 h. The molecular weights of

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the P(ET-co-HB)-50/50 and the two fractions are
given in Table 1.

Table 1: Molecular weights of the P(ET-co-HB)-50/50
copolyester and the two fractions

	$\overline{M_n}^*$ g/mol	$\overline{M_w}^*$ g/mol	$\overline{M_w}/\overline{M_n}^*$	$\overline{M_\eta}^{**}$ g/mol
P(ET-co-HB)-50/50	2.4×10^4	7.4×10^4	3.1	1.1×10^4
chloroform soluble fraction	1.9×10^4	4.2×10^4	2.2	—
chloroform insoluble fraction	2.4×10^4	9.0×10^4	3.8	—

 * estimated by GPC using polystyrene standards

** estimated from the relation $\eta = 1.23 \times 10^{-3} M_n^{-0.66}$ /14/

Equipment: The morphology was observed by a phase contrast
microscope (Carl-Zeiss-Jena) with crossed polari-
zer and analyser. For the studies at elevated
temperatures a LINKAM temperature cell THM 600
was used. The C^{13}-spectra were obtained on a Bruker-
Spectrospin MSL 300 spectrometer using $CDCl_3$/hexa-
fluoroisopropanol (50:50 wt%) as a solvent.
$Cu(AcAc)_3$ was used to shorten the relaxation time.
The peak area separation was carried out with
the program Linesim.

RESULTS AND DISCUSSION

Figure 1 shows the morphology of the P(ET-co-HB)-50/50
copolyester after annealing at 260°C for 80s.
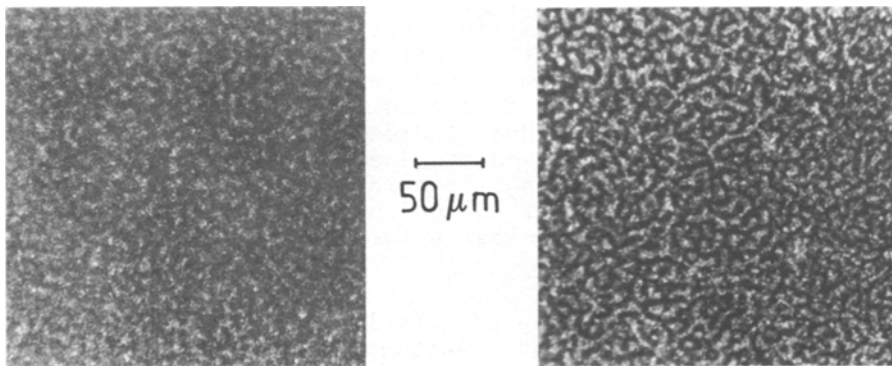
a) P(ET-co-HB)-50/50   b) P(ET-co-HB)-60/40 blended
                                   with PET (50:50 wt%)

Figure 1: Morphology of thin as-cast films annealed at 260°C
for 80s.

Indeed, for the copolyester a morphology is observed as it
is characteristic for spinodal unmixing of a polymer mixture.
For a comparision Figure 1b reveals the structures which accom-
pany the spinodal decomposition in blends of P(ET-co-HB)-60/40/
PET (blending ratio 50/50 wt%) as described elsewhere /15,16/.
Obviously, spinodal decomposition is bound up with multicompo-
nent systems and cannot occur in a copolymer itself. Therefore,
a fractionation of the copolyester with chloroform was carried
out. Figure 2 depicts the GPC curves of the copolyester and
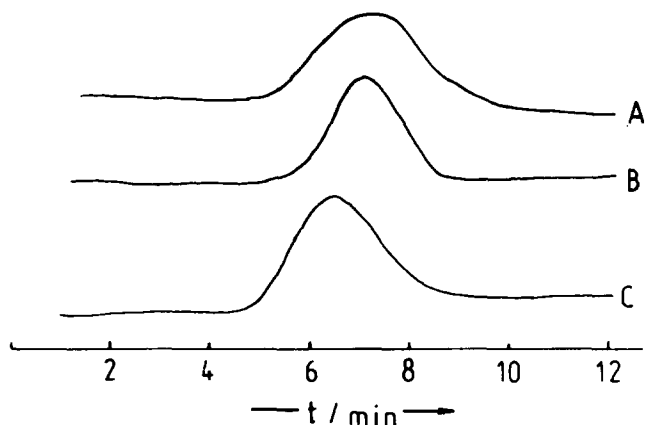the two fractions.

Figure 2: GPC traces of the P(ET-co-HB)-50/50 copolyester
           (A), the chloroform soluble fraction (B) and the
           insoluble fraction (C).

It can be seen that the chloroform insoluble fraction has
a somewhat higher molecular weight than the soluble fraction.
But the fractionation is mainly carried out with respect to
the chemical structure of the copolyester rather than the
molecular mass. This can be demonstrated by the completely
different morphologies and the phase behavior of the fractions
(cf. Fig. 3). The chloroform soluble fraction shows spherulites
which seem to be disturbed by a second phase. Also the inso-
luble fraction consists likely of more than one phase. These
results are in agreement with DSC-measurements by Quach et
al. /10/.
    Also the phase behavior at high temperatures is completety
different. The soluble fraction shows an isotropic behavior
above the melting point. The insoluble fraction exhibits at
elevated temperatures the typical structures of a nematic
phase. However, the structures accompanying spinodal decompo-
sition do not appear.

a) chloroform soluble
    fraction

b) chloroform insoluble
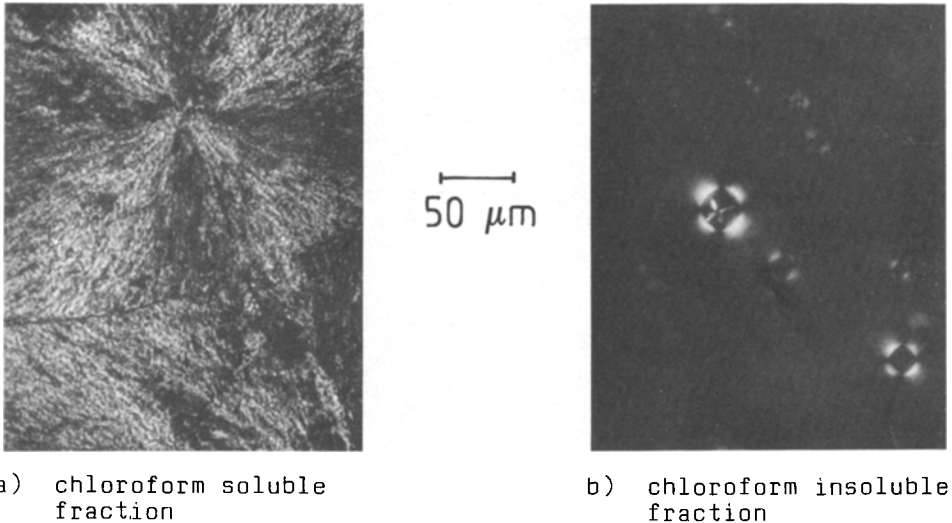   fraction

Fig.3: Morphology of thin as-cast films of the two fractions
        at room temperature

        To get more insight into the chemical nature of the
fractions a sequence analysis based on C^{13}-NMR measurements
was carried out. Figure 4 shows the C^{13}-NMR spectra of the
copolyester and the two fractions. The peaks ranging from
130.0 to 130.8 ppm correspond to the CH-carbon atoms of the
terephthalate moieties (cf. Ref./13/). The splitting into
four peaks is caused by three different triades (OTO, OTE
and ETE; O-oxybenzoate, T-terephthalate and E-ethylene).
Owing to the asymmetry of the OTE-triade two peaks appear.
The peaks in the range from 122.0 to 122.4 ppm refer to the
O-centered triades (OOO, TOO; OOE and TOE) /13/. The chemi-
cal compositions of the copolyester and the two fractions
were estimated using the integral ratio of the two peak
groups (cf. Tab.2). For the copolyester the 50:50 composition
was confirmed whereas the insoluble and soluble fractions
contain 61 % and 39 % HB, respectively. Table 2 shows the
experimentally determined and the calculated relative peak
areas of the triades. The calculated values were obtained
for the case of a random copolymer, i.e., all bonding proba-
bilities are equal /13,17/. It can be seen that deviations
from the randomness exist which are somewhat higher for the
chloroform insoluble fraction as for the soluble fraction.
This may agree with findings of Nicely et al. /12/ that de-
viations from randomness are more pronounced at higher HB-
contents. Furthermore, it should be noticed that the T-cen-
tered triades exhibit higher deviations than the O-centered
triades. As a result the soluble as well as the insoluble
fraction are not really random copolymers but tend slightly
to multiblock systems.

In conclusion, the phase separation detected in the
50/50 copolyester is caused dominantly by the different
compositions of the constituents. The slightly "blocky" na-
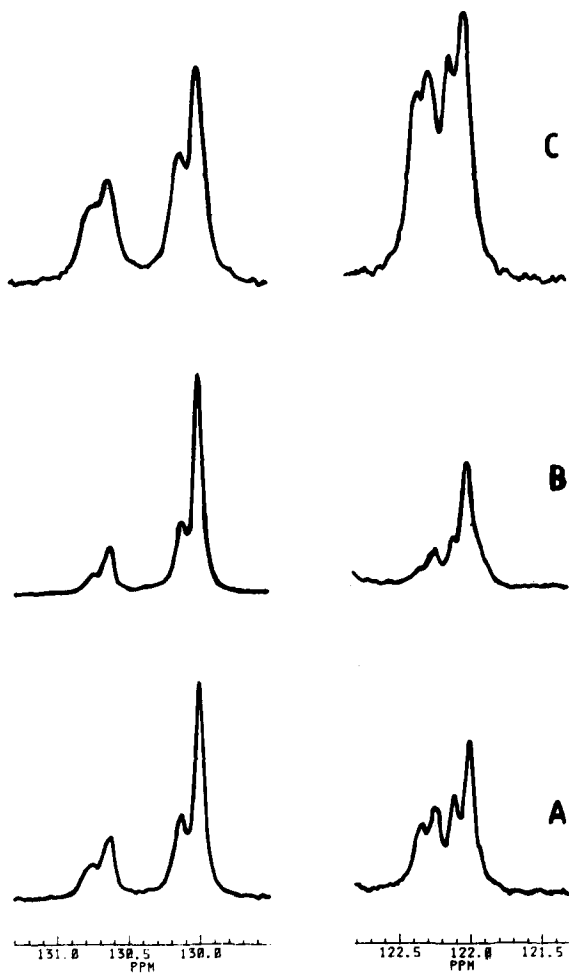ture of the copolyesters is of minor influence.

131.0 130.5 130.0
PPM

122.5 122.0 121.5
PPM

Fig.4: C^{13}-NMR spectra of the copolyester (A), of the
soluble fraction (B) and the insoluble fraction (C).
The peaks ranging from 122.0 to 122.4 ppm are
enlarged vertically by a factor 2.

Table 2: Calculated (after/13/) and by C^{13}-NMR data experimentally determined peak areas of the different triades for the two fractions.

triade	δ/ppm	soluble fraction 39 % HB			insoluble fraction 61 % HB		
		experimental	calculated	integral peak area	experimental	calculated	integral-peak area
TOE	122.0	59.7	57.4		33.4	31.4	
OOE	122.1	17.9	18.4	11.8	23.4	24.6	3.5
TOO	122.3	15.4	18.4		22.4	24.6	
OOO	122.4	7.0	5.8		20.8	19.4	
OTO	130.8	4.4	5.8		13.6	19.4	
OTE (C-4)	130.6	13.6	18.4	9.2	20.3	24.6	1.1
OTE (C-3)	130.1	16.9	18.4		20.6	24.6	
ETE	130.0	65.1	57.4		45.5	31.4	

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