

# Investigations of the hardness and thermal properties of copoly(ether-ester)s containing segments of different molecular weights

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Copoly(ether-ester)s (CPPE) consisting of alternately arranged oligooxyethylene (PEO) soft segments of molecular weights 400 to 6000 and tetramethylene-terephthalate (4GT) hard segments was studied. The content of soft segments of copoly(ether-ester)s obtained varied over a wide range. Differential scanning calorimetry and hardness measurements in the temperature range from  $-70$  to  $+150^{\circ}\text{C}$  were carried out. At temperatures close to the melting point a significant change in hardness of CPPE occurs. This does not occur in those elastomers for which the enthalpy of melting ( $H_m$ ) of the soft segments approaches zero.

(Keywords: copoly(ether-ester)s; hardness; oligooxyethylenediol; poly(butylene-terephthalate); polycondensation)

## INTRODUCTION

The influence of temperature on hardness of copoly(ether-ester)s (CPEE) containing both hard and soft segments was studied. These polymers are segment elastomers of significant block compatibility<sup>1-7</sup>.

The content of segments in the synthesized polymers was calculated on the basis of the conventional definition. According to that definition, a soft segment consists of one poly(ethylene oxide) (PEO) sequence and one terephthalate sequence.

Polyethers, particularly polyoxyethylene-ethers, show the ability to crystallize. The temperature and heat of crystallization depends on the structure and molecular weight of the polyether. Thus the mechanical properties of CPEE, including the hardness should also depend on the ability of the soft segments to crystallize. In this work, the hardness of CPEE copolymers containing soft segments with different abilities to crystallize (i.e. different values of  $T_m$  and  $\Delta H_m$ ) was examined.

## EXPERIMENTAL

### Materials

Copoly(ether-ester)s were synthesized via transesterification and polycondensation in the melt, using oligooxyethylenediols received from Hoechst Aktiengesellschaft. Molecular weights of the CPEE obtained ranged from 20 000 to 30 000 g/mol. Conventional catalyst and amine stabilizers were used.

### Sample preparation

The samples were prepared for d.s.c. examination by press moulding. Samples for hardness tests were prepared by injection moulding. Press moulding was carried out at a temperature of  $25^{\circ}\text{C}$  higher than the melting point ( $T_i$ ) determined using a Bötius apparatus (Table 1). The press moulding pressure was 35 MPa. The samples, which were 80 mm in diameter and 0.5 mm thick, were placed

in the press for three minutes, quenched at a rate approximately  $15^{\circ}\text{C}/\text{min}$  and stored in an inert gas atmosphere at room temperature.

The samples for hardness determination were obtained by injection moulding using die temperatures approximately  $5^{\circ}\text{C}$  higher than  $T_i$  (Table 1) at pressure of around 50 MPa. The specimens obtained were 50 mm in diameter and 6 mm thick.

### Differential scanning calorimetry

Measurements of thermal properties were carried out using a Perkin-Elmer (DSC-2) differential scanning calorimeter and a heating rate of  $10^{\circ}\text{C}/\text{min}$ . The weight of the sample varied between 19–26 mg.

### Measurements of polymer melting points ( $T_i$ )

Measurements of  $T_i$  for the copoly(ether-ester)s were carried out using a Bötius microscope of HMK type from Franz Kustner Nacht KG. The heating rate was  $4^{\circ}\text{C}/\text{min}$ . The temperature was determined when the irregular contours of the polymer assumed the shape of a drop.

### Measurements of hardness (H)

Hardness measurements were performed using Shore D apparatus (Carl Frank GMBH type 104) according to standard DIN 5305. The hardness tester was placed in a chamber whose temperature could be adjustable in the range  $-70$  to  $+200^{\circ}\text{C}$ . Before the measurement, the samples were thermostated for 30 min. The apparatus was calibrated at the measurement temperature.

## RESULTS AND DISCUSSION

It has been assumed that a change in the structure of the polymer combined with a change in the content and size of the segments should influence its useful properties<sup>3,8</sup> including, e.g. hardness of copoly(ether-ester)s.

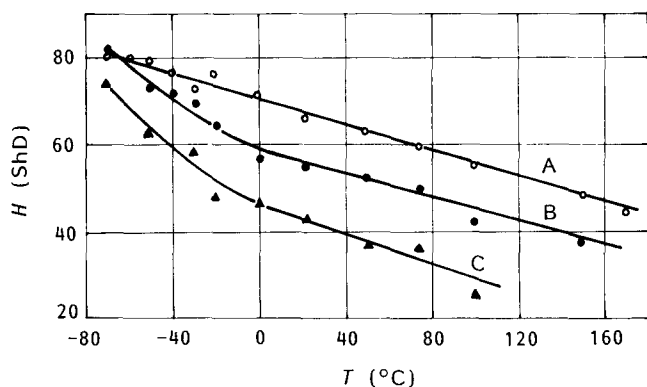
**Table 1** The thermal properties of the samples

Sample	Molecular weight PEO (g/mol)	Soft segment content (wt%)	$T_m$ (°C)	$H_m$ (J/g)	$T_c$ (°C)	$T_i$ (°C)
A	400	20	—	—	—	220
B		40	—	—	—	201
C		60	—	—	—	170
D	1000	20	—	—	—	225
E		40	—	—	—	208
F		60	0	14	-28	183
G		70	8	27	-14	166
H		80	15	43	-2	135
I	6000	20	20	50	-32	235
J		40	33	65	3	232
K		60	44	89	24	221
L		80	52	112	30	190
M		85	54	114	32	180

 $T_m$ —melting point of soft segment

 $H_m$ —crystallization heat of soft segment

 $T_c$ —crystallization temperature of soft segment

 $T_i$ —melting point of polymer

**Figure 1** Influence of temperature on hardness of copoly(ether-ester)s with soft segments of MW 400

To prove the above assumption, a series of syntheses was carried out. In the syntheses, in addition to the hard crystalline segments, soft crystallizing segments were also produced. The molecular weight of the soft segments was changed (PEO 400, PEO 1000 and PEO 6000). Its content was also changed (20–85 wt%). For the polymers obtained, the thermal properties ( $T_m$ ,  $T_c$  and  $\Delta H_m$ ) and the hardness, corresponding to the different values of the thermal properties temperatures, were determined. It was found that an increase in PEO content in the polymer at constant PEO molecular weight causes an increase in  $T_m$  and  $\Delta H_m$ .

On the d.s.c. diagrams of the polymers obtained with PEO segments of molecular weight 400 (A, B and C polymers in Table 1) the characteristic peaks for soft segments melting and crystallizing have not been observed. CPEE containing PEO 1000 (D to H polymers in Table 1) appear to have measurable values of  $T_m$  and  $T_c$  beyond a 50% content of soft segments. The polymers containing PEO 6000 segments (I to M in Table 1) have  $T_m$  and  $T_c$  values measurable for all the investigated soft segments contents.

Next, the melting points of the investigated polymers were compared with hardness values measured at different temperatures. It has been observed that at temperatures lower than  $T_m$  (Figures 2 and 3) the polymers appear to

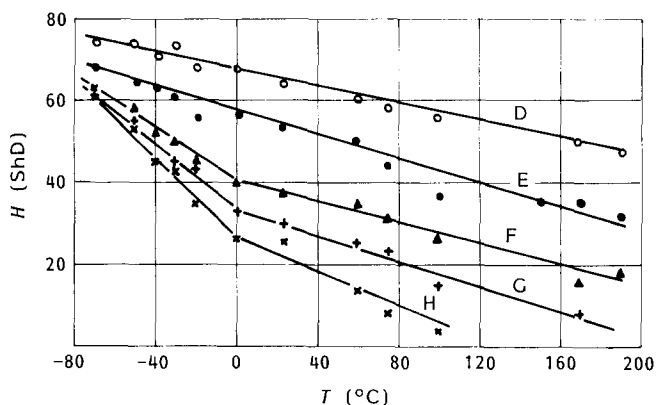
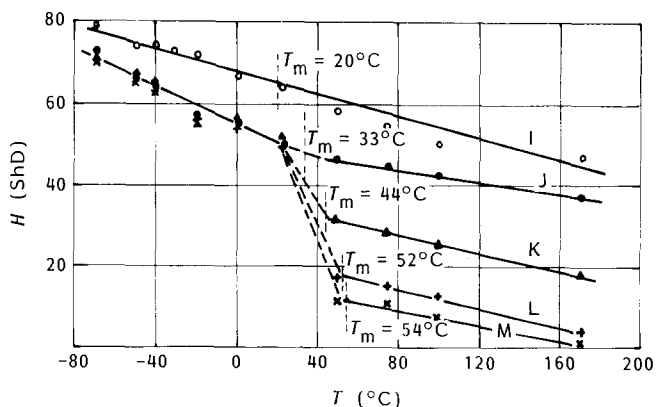
have approximately the same (curves F, G, H) or identical (curves J, K, L, M) hardness values. Figure 2 shows that at temperatures lower than  $T_m$  the distance between the F, G, H curves decreases with the measurement temperature. The J, K, L, M curves in Figure 3 overlap forming one curve below the melting point of the soft segments.

At the temperatures above  $T_m$ , the polymers investigated, with respect to the content and molecular weight of PEO, have different hardness values (Figures 2 and 3).

At temperatures close to  $T_m$  the curves of polymers F, G, H, J, K, L and M are discontinuous. Polymers A, B, C obtained using PEO 400, and polymers D and E obtained using PEO 1000, show neither the ability of the soft segments to crystallize (Table 1) nor the discontinuity (Figures 1 and 2). Polymer I, containing PEO 6000 soft segments, is an exception for which a considerable melting heat of the soft segments and linear dependence of hardness on measurement temperature are observed. Because this polymer has statistically less than one PEO block per macromolecule (20 wt%) it should be considered as a modified polymer rather than a block polymer.

The higher the melting heat of the soft segments the larger the change in hardness for polymers F, G, H, J, K, L, M.

The shifting of melting point and crystallization temperature towards lower temperatures and lowering of  $\Delta H_m$  (Table 1) indicates that an increase in the 4 GT content in the polymer causes soft segment disturbances. The hardness changes in a similar way. The temperature at which the large change in hardness occurs also shifts


**Figure 2** Influence of temperature on hardness of copoly(ether-ester)s with soft segments of MW 1000

**Figure 3** Influence of temperature on hardness of copoly(ether-ester)s with soft segments of MW 6000

towards lower temperatures, respectively, to the decrease in PEO content in CPEE.

The melting point of the soft segment and the resulting change in hardness also depends on the molecular weight of the PEO used for the synthesis. The higher the molecular weight of the 4 GT blocks the lower the miscibility of the 4 GT blocks in PEO.

The decrease in the disturbance of the soft segments by the 4 GT short sequences, as the miscibility of the soft and hard segments decreases, produces an increase in  $\Delta H_m$ ,  $T_m$  and  $T_c$  for the soft segments.

The observed correlation between the changes in hardness and melting points of the soft segments in copoly(ether-ester)s is of significance with regard to their uses.

#### ACKNOWLEDGEMENT

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