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Ordered structure in polyester elastomers containing quaterphenyl group

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Summary

By use of DSC, X-ray diffraction and dynamic mechanical spectroscopies, phase separation and ordered structure were investigated for 4, 4'''-dihydroxy-p-quaterphenyl /ethylene glycol/adipic acid copolymers (xDHQ copolyesters, x: DHQ content in mol%, $0<x\leqq 10$). The xDHQ copolyesters are distinctly phase-separated into two phases, rigid DHQ and soft PEA phases. The PEA phase were partially crystalline, and showed glass transition near 240 K and melting of PEA crystallites near 280 K. In the DHQ phase, DHQ segments were ordered in layered structure at room temperature.

Introduction

Copolyesters consisted of hard and soft segments are important polymeric materials which have been widely used as high strength engineering plastics (1–5) and thermoplastic elastomers (6–10). Recently, Niki et. al. (11–13) gave an eye to 4, 4'''-dihydroxy-p-quaterphenyl (DHQ) as a hard segment of thermoplastic elastomers, and developed DHQ/ ethylene glycol/adipic acid copolymers (Fig. 1)(hereafter denoted as xDHQ copolyester, x: DHQ content in mol%, $0<x\leqq 10$). They reported that the xDHQ copolyesters are excellent thermoplastic elastomers and suggested that DHQ segments are phase-separated from poly(ethylene adipate)(PEA) region to form crystalline domains, which act as rigid crosslinks, even in low DHQ contents from 2 through 10 mol%. Rather unexpectedly, however, PEA phase was almost amorphous at room temperature and the DHQ crystallites were gradually disturbed with increasing temperature to 550 K, showing no distinct melting point. DHQ is certainly attractive and unique comonomer as a hard component for elastomers, because it is rigid and slender, and mesogenic compound (14, 15). Therefore, it is important to disclose the structural and physical characterizations of xDHQ copolyesters.

The present paper briefly communicates our new findings on phase-separation and ordered structures of the xDHQ copolyesters: Not only DHQ but also PEA phases are crystalline and show interesting melting behavior.

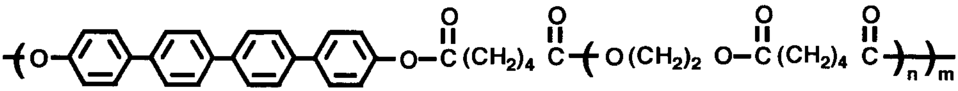

Fig. 1. Chemical structure of xDHQ copolyesters (x: DHQ content in mol%, x =2.5, 3.75, 5.0, 7.5 and 10 mol%). The sum of DHQ(x) and ethylene glycol contents = 50 mol% and adipic acid content = 50 mol%.

Experimental

The DHQ copolyesters were kindly supplied from Sekisui Chemical Co., Ltd.: The copolyesters were synthesized by a melt condensation polymerization of 4, 4'''-dihydroxy-p-quaterphenyl, ethylene glycol and dimethyl adipate at 453–573 K (11). The limiting viscosities for all the DHQ copolyesters laid between 0.5–1.2 in o-chlorophenol at 303 K (11). The DHQ polyesters obtained were compression-molded into sheets of about 1 mm thick around 513 K and cooled to room temperature with cold water.

Differential scanning calorimetric (DSC) measurements were carried out with a Perkin-Elmer DSC-7 calorimeter at a heating/cooling rate of 10 K•min^{-1}. X-ray diffraction experiments were made by a diffractometer (Rigaku, CN2155R5) equipped with a temperature controller (Rigaku, CN2352A221), using monochromated Co Kα radiation (λ=1.790Å)(Rigaku, RU-200B). Dynamic mechanical measurements were performed at about 0.2–3 Hz and in the temperature range of 140–580 K with a torsion pendulum method by use of a Resuka RD-1100AD instrument .

Results and Discussion

Figure 2 shows DSC 2nd-heating curves for xDHQ copolyesters. In the x=2.5 mol% copolyester, the curve shows an abrupt change near 240 K and two peaks near 288 (peak A) and 327 K (peak B). The change near 240 K is seen for all the xDHQ copolyesters and may be attributed to a glass transition in PEA phase, which is also evidenced with dynamic mechanical results described later. As DHQ content (x) increases, the peak A becomes smaller in intensity and is scarcely seen at 7.5 mol% of x. On the other hand, the peak B is small but exists for all the xDHQ copolyesters, independent of x.

Figure 3 shows X-ray diffraction patterns for xDHQ copolyesters. In the wide angle region for the x=2.5 mol% copolyester (Fig. 3 (a)), the pattern shows five diffraction peaks at about 23.0, 25.2, 26.9, 28.6 and 32.6° at ①303 K (virgin sample). Referring to the X-ray diffraction data by Niki et. al. (12, 13), three peaks at about 23.0, 26.9 and 32.6°, and two peaks at about 25.2 and 28.6° are attributable to those originating in DHQ crystallites and PEA crystallites, respectively. The three DHQ peaks existed for all the xDHQ copolyesters but the two PEA peaks were scarcely observed for the copolyesters of the higher DHQ contents than 5.0 mol%. When temperature elevates from ①303 to ②343 K (1st-heating), the PEA peaks disappear but the DHQ peaks exist. When temperature is cooled from ②343 K (1st-cooling), the PEA peaks faintly reappears at ③303 K and is distinctly visualized at ④253 K. When temperature increases from ④253 K again (2nd-heating), the PEA peaks largely decrease in intensity

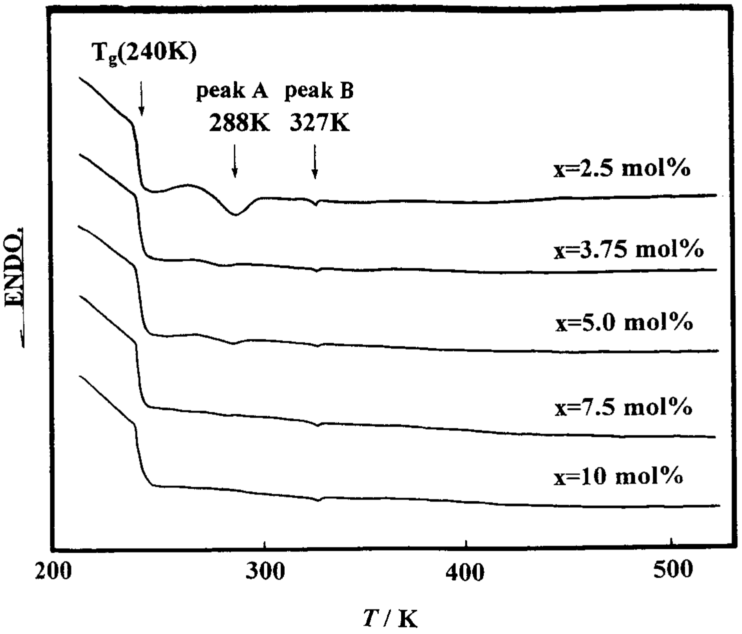

Fig.2. DSC 2nd-heating curves for xDHQ copolyesters.

at ⑤303 K (the temperature between the peak A and B in Fig. 2) and disappears at ⑥343 K (above the temperature of the peak B in Fig. 2). On the other hand, the DHQ peaks exist at all the thermal stages. DHQ segments work as physical crosslinks, and the PEA segments attached to the DHQ segments are considered to be ordered partially. Therefore, PEA peaks may be observed at 303 K and this PEA segments melt at peak B. These X-ray data indicate that the peak A may be caused by the melting of the PEA

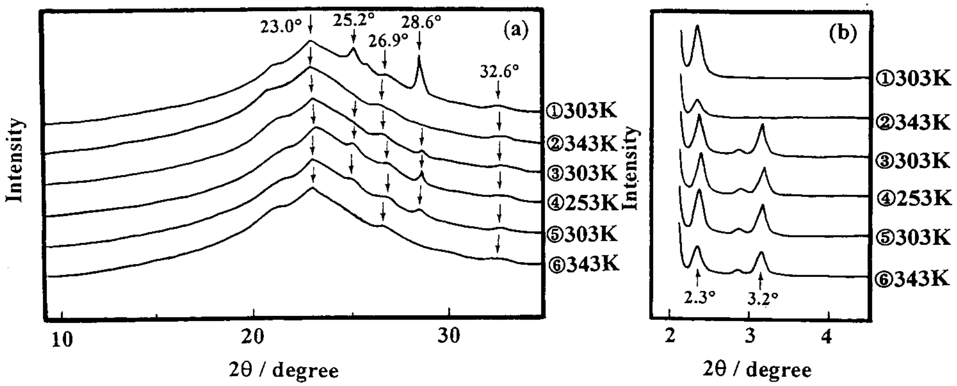

Fig.3. X-ray diffraction patterns for the xDHQ copolyesters: (a)x=2.5 mol% (wide angle region), (b)x=7.5 mol% (small angle region).

crystallites, which would not be restricted by DHQ crosslinks, in PEA phase. Niki et al. (11) found that the x=5.0 mol% copolyester has a peak near 0.75° (137 Å) on the small angle X-ray scattering (SAXS) at room temperature. In Fig. 3 (b), the X-ray diffraction data in the small angle region for the 7.5 mol% copolyester show two peaks near 2.3° (45 Å) and 3.2° (32 Å) which may correspond to the higher order reflections (the third and fourth order, respectively) of the 0.75° peak. From these X-ray results, it can be deduced that DHQ and PEA segments are ordered together with PEA segments attached to DHQ segments to form a lamellar structure, since the DHQ moiety is estimated to be about 18.5 Å long in the extended chains. In Fig. 3 (b), these two peaks are smaller and broadened at ⑥343 K, accompanied with the loss of PEA peaks at 25.2 and 28.6° and this suggests that the lamellar structure are somewhat disturbed between ⑤303 and ⑥343 K. Another weak peak is observed at about 2.9° (35 Å). This peak is presumed to correspond to the higher order reflection of a certain long spacing, but we could not assigned it any longer now. Consequently, we speculate the structure of DHQ phase as follows: At room temperature, the lamellar structure is formed by both DHQ and PEA segments. DHQ moieties are packed each other to form one layer and the DHQ layers are sandwiched with ordered PEA segments to construct the layered structure; PEA segments attached to DHQ would be ordered, although PEA segments apart from DHQ

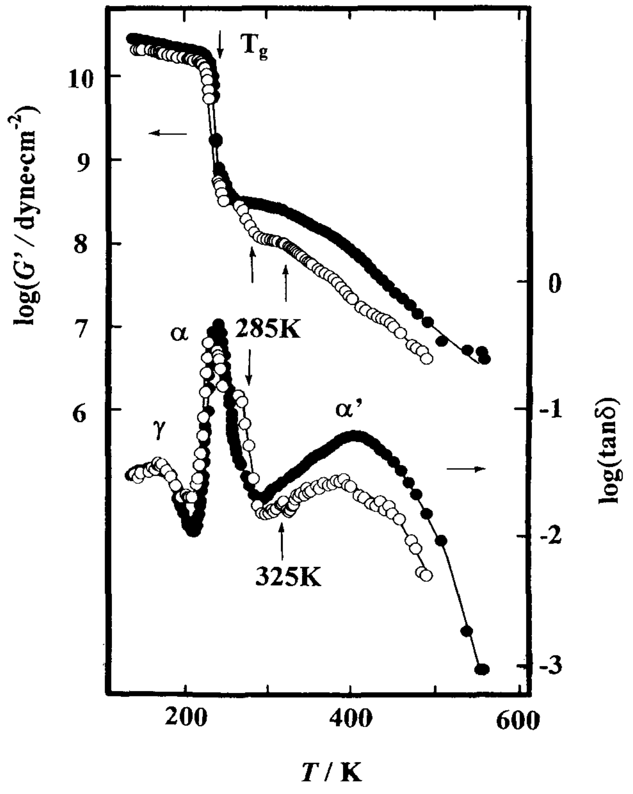

Fig.4. Temperature dependence of storage elastic constant (G') and the loss tangent (tanδ) for xDHQ copolyesters. ○: x=3.75 mol%, ●: x=10 mol%.

would be less ordered, resulting in the faint X-ray reflections at 25.2 and 28.6° at ⑤303 K. When temperature increases, the ordered PEA segments in the vicinity of the layered DHQ crystallites are disordered near 327 K, at which the DSC curve shows one small endothermic peak (peak B in Fig. 2), and the layered orderliness of DHQ segments seem to somewhat decrease.

Figure 4 shows temperature dependence of storage elastic constant (*G'*) and the loss tangent (tanδ) for 3.75 and 10 mol% DHQ copolyesters. There are observed two relaxational peaks, γ and α peaks near 190 and 245 K, which may be related to a local molecular motion of short segments below T_g (242 K) and a reorientational molecular motion of long segments above T_g, respectively. In addition to the two relaxations, two discontinuous change are observed near 285 and 325 K. Apparently, the 285 and 325 K changes respond to the melting of PEA crystallites in PEA phase and the decreasing of the layered orderliness in DHQ phase, respectively. The shoulder in *G'* at around 270 K seems to correspond to the recrystallization of PEA block. It is noted that a large relaxational peak (α' relaxation) appears in a wide temperature range above 300 K. By X-ray diffraction studies, it has been pointed out, as already described, that the DHQ layered orderliness in DHQ phase is gradually disturbed, as temperature increases, and mostly lost near 555 K. In Fig. 2, DSC curves appear to undergo a very small and gradual change in the wide temperature range from 350 to 500 K. These results indicate that the broad mechanical relaxation peak in the higher temperature range might respond to a gradual relaxing of orderliness in DHQ crystallites.

Further detailed structural studies are in progress and will be published elsewhere in the near future.

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