Microphase separation behaviour in a series of thermotropic liquid crystalline copolyethers

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The phase transition and microphase separation behaviour have been studied by means of differential scanning calorimetry, polarizing microscopy, depolarizing transmittance and X-ray diffraction measurements for a series of thermotropic liquid crystalline random copolyethers. These are composed of two similar aromatic azomethine ether units, derived from 3,3′-dimethoxy-4,4′-diformyl-α,ω-diphenoxyhexane with 4,4′-diaminodiphenylmethane (system A) and with 4,4′-phenylenediamine (system B). These copolymers, with the exception of those containing a high content of the A component, were found to transform from a crystalline to a nematic liquid crystalline, and finally to an isotropic phase. For the specimens with 40, 50 and 60 mol% of the A component a microphase separation phenomenon was distinctly observed: segments of the A and B components along the polymer backbones may separately form their own crystalline domains, which melt in different temperature ranges. After this, the A domains are transformed directly into the isotropic state, while the B segments can still form special mesomorphic domains. A phase diagram for these copolymers was also obtained: the melting points of the crystalline domains formed by segments of the A component were found to be only slightly changed with variation in the component content, while the melting and the isotropization transition temperatures of the B component domains were lowered significantly with decreases in the B component content.

(Keywords: liquid crystalline copolymers; phase transition; microphase separation)

INTRODUCTION

Liquid crystalline polymers (LCPs) have recently attracted a great deal of attention because of their excellent physical properties and potential for use in various application areas. Considerable work has been done in recent years in synthesizing new homopolymers or copolymers which can exist in different types of mesophase and to examine the possibility of using these LCPs as structural or functional materials. The structure and properties of liquid-crystal forming polymers are much more complicated than those of conventional polymers, due to their mesomorphic behaviour, so it becomes important to expand our knowledge of polymer science, developed basically on studies of structure and properties of conventional polymers, to cover the new field of LCPs.

It is well known from studies of conventional polymers that microphase separation may occur in copolymer samples when their components are not miscible. The dispersion state of the components in the crystalline and amorphous phases is an important structural characteristic of copolymers and has an obvious influence on their properties. It is of great interest, therefore, to study the microphase separation behaviour of liquid crystalline copolymers.

Poly(ethylene terephthalate) (PET) and p-hydroxybenzoic acid (PHBA) form a typical thermotropic liquid crystalline copolymer which has been studied by many workers[1–5]. For this copolyester, a biphasic structure, or the so-called microphase separation phenomenon, was observed. Such a separation behaviour was found to be very sensitive to the PET or PHB content, as well as the moulding temperature used in compressing the film. Several other types of liquid crystalline copolymers were studied[6–8], some of which showed microphase separation behaviour, while others did not. In these studies, the occurrence of microphase separation was associated with a non-random distribution, along the polymer backbone, of monomer segments of the different components, while the monomer chain distribution was random for a non-separated phase system.

We have synthesized a new series of thermotropic liquid crystalline copolyethers, in which the different monomer units have similar chemical structures but quite different spatial morphologies. In this paper, we will examine whether each component can form its own special crystalline or liquid crystalline domains. We will also discuss the influences of the component composition

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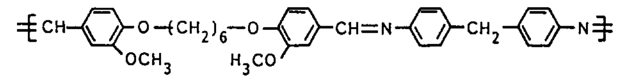
and the segment length on the phase transition behaviour and liquid crystallinity of the samples.

EXPERIMENTAL

Materials

A series of thermotropic, liquid crystalline copolyethers with the following (similar) aromatic azomethine ether units was synthesized:

A


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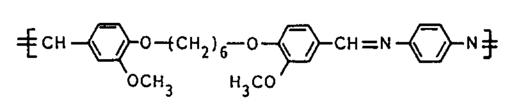

In this study, specimens with unit A contents of 0, 20, 40, 50, 60, 80 and 100 mol% were utilized for structure and thermal transition analyses. The procedures adopted for copolymerization are briefly described below.

The monomer, 3,3′-dimethoxy-4,4′-diformyl-α,ω-diphenoxyhexane, was prepared by a condensation reaction (at room temperature for ~4 h) between 1,6-dibromohexane and vanillin in DMF, in the presence of anhydrous Na_2CO_3. The copolyethers were then obtained by a polycondensation reaction of the resulting dialdehyde with 4,4′-diaminodiphenylmethane and 4,4′-phenylenediamine in different molar ratios, which was carried out under a nitrogen atmosphere at ~110°C for 4 h, with acetic acid as catalyst. By taking into consideration the almost equal activation energies for reaction of the two diamines, plus the equal probability of them reacting with the dialdehyde, then the copolymers that are finally obtained can be reasonably assumed to be random ones. For these copolyethers, any information concerning molecular weight, segment length of each component and the relevant distributions, however, was difficult to obtain, due to their very poor solubilities in organic solvents.

Measurements

The thermal transition behaviour was determined with a Perkin–Elmer DSC-4 differential scanning calorimeter. The instrument was linked on-line to a computer that allowed the output to be corrected for baseline curvature and to be calibrated in absolute units. Heating and cooling rates of $20°C\,min^{-1}$ were used. Optical microscopic observations were performed with an Olympus BHSP polarizing microscope, equipped with a hot stage. The temperature dependence of the depolarizing transmittance of the specimens was indirectly measured using an Olympus PM-10AD automatic exposure unit attached to the microscope. In these measurements, the reciprocal of the exposure time was expected to be proportional to the brightness, or the intensity of light transmitted through the sample. X-ray diffraction patterns were recorded by a Rigaku D/max-γA diffractometer (40 kV, 150 mA) using graphite monochromatized CuKα radiation ($\lambda = 1.5418$ Å).

RESULTS AND DISCUSSION

In order to clarify whether or not the synthesized materials are physical mixtures of the A and B homopolymers, we have measured and compared the infra-red spectra and d.s.c. thermograms for all of the samples, as well as blends of the two homopolymers. It was found that spectra of the various copolymers are not just coincident with a simple superimposed spectral pattern of the two homopolymers. Curve (b) in *Figure 1* shows the d.s.c. thermogram of a sample which has been prepared by simply mixing the two homopolymers in the same molar ratio, within their isotropic phase temperature range, and then subsequently slowly cooling to room temperature. For comparison, the curve of a 50 mol% sample, again cooled from the isotropic state is also presented (curve a). The former samples are semicrystalline with crystallinities that are much lower than those of the synthesized ones. In addition, they melt at temperatures that are more or less lower than those of the as-synthesized specimens (see *Figure 2* below). From *Figure 1* we can also see the essentially different thermal behaviour between this copolymer and the (physically) mixed homopolymers, although they have been annealed, or mixed, under the same conditions. From such observations, it seems, therefore, quite justifiable to regard these as-synthesized specimens as being copolymers.

By carefully carrying out polarizing microscopic observations and small angle light scattering measurements, we have found that at high temperatures these specimens, except for those with high contents of component A, may transform from the crystalline (K), to the nematic liquid-crystalline (N), and finally to the isotropic phase. *Figure 2* shows the d.s.c. thermograms obtained on heating the seven as-synthesized copolymers. It is clear that the endothermic peaks shift their positions towards the lower temperature side as the A component content

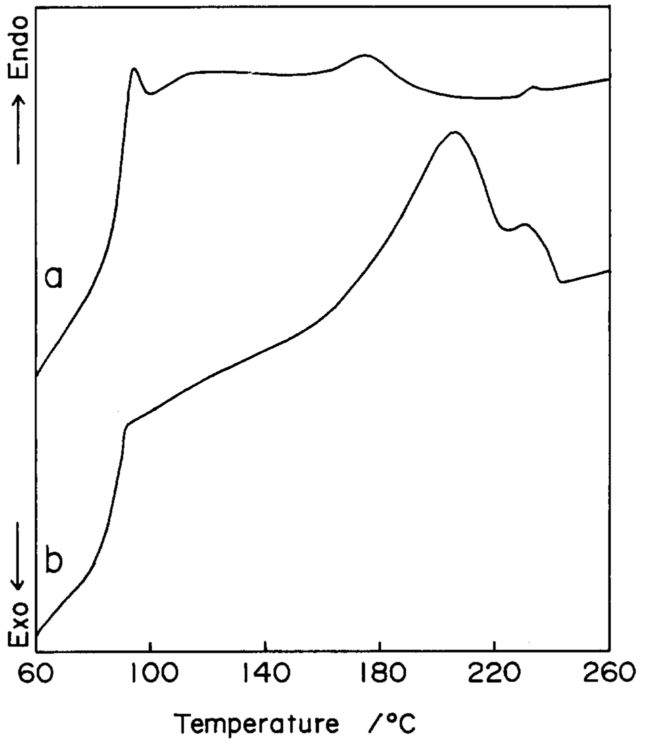

Figure 1 D.s.c. thermograms of (a) a liquid crystalline copolymer containing 50 mol% of component A and (b) a sample prepared by physically mixing equal molar ratios of the two homopolymers A and B, with specimens having been cooled from the isotropic state in both cases

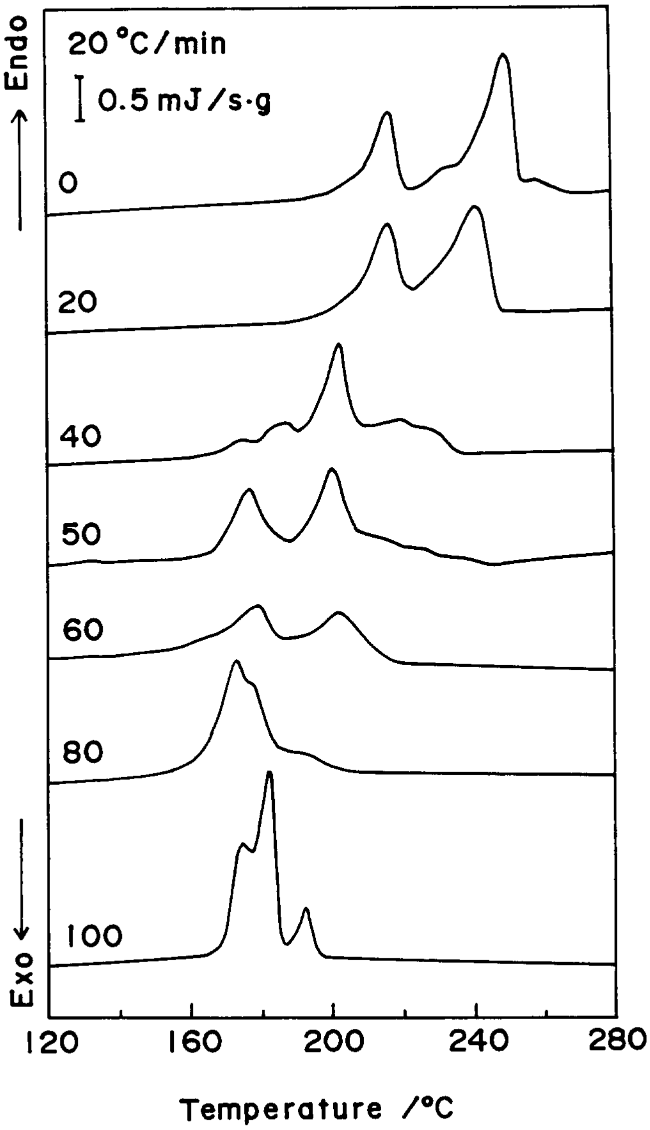

Figure 2 D.s.c. thermograms of the seven as-synthesized copolymer samples where figures by each curve indicate the content (mol%) of component A

increases, although the details are quite complicated (as described below).

Specimens containing 0 and 20 mol% of component A

We describe here the phase transition behaviour of 0 and 20 mol% A (100 and 80 mol% B) component specimens. As seen in *Figure 2*, there are four endothermic peaks, namely two large (217 and 250°C) and two small (233 and 259°C), in the d.s.c. curve of the 0 mol% A sample. *Figure 3* shows the temperature dependence of the depolarizing transmittance of these two samples with heating. In the 0 mol% A specimen, the transmittance starts to increase at about a temperature corresponding to the 250°C d.s.c. endothermic peak, and after reaching a maximum at ~259°C (c.f. d.s.c. peak) it then decreases rapidly. In combination with optical microscopic observations (photographs not shown here), we found that the sample melts and forms the N phase at ~250°C, and further transforms to the isotropic state at ~260°C, with the two transition processes corresponding well to two of the d.s.c. endothermic peaks. However, we could not observe any appreciable changes occurring in either the transmittance or optical texture corresponding to the 217°C d.s.c. peak temperature, although this transition was accompanied by quite a large enthalpy change. What structural change occurs at this transition is not very clear at present, but it is probably associated with a partial melting or a phase transition in the solid state.

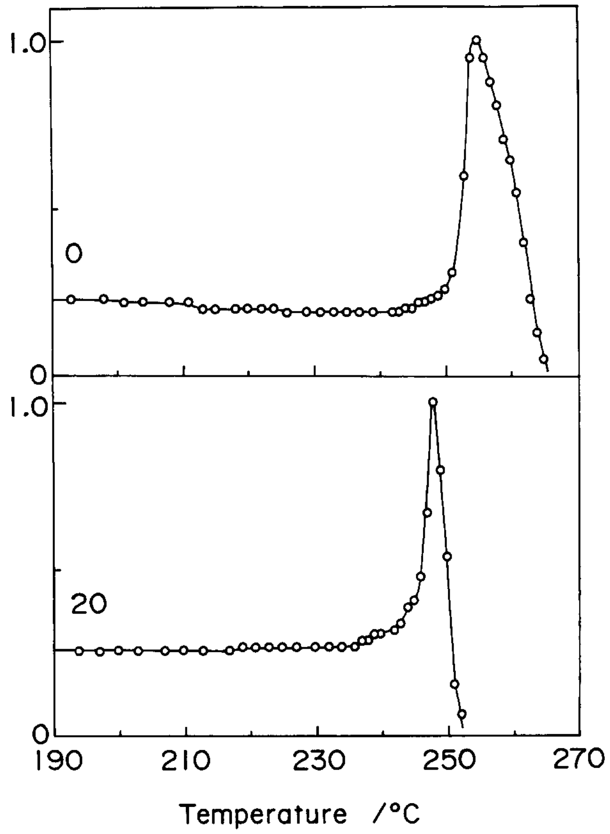

Figure 3 Temperature dependence of the depolarizing transmittance of copolymer samples containing 0 (top curve) and 20 (bottom curve) mol% of component A

Similar observations have been made in the case of the 20 mol% A specimen. From the transmittance change and optical microscopic observations, we found that the d.s.c. peak on the higher temperature side (241°C) may be related to a K–N phase transition, while no large change in the optical properties was observed corresponding to the peak on the lower temperature side (216°C).

Specimens containing 40, 50 and 60 mol% of component A

With these specimens it is preferable to study the liquid crystallinity and the miscibility between the different components, because these copolyethers have A and B contents which are close to each other. As seen in *Figure 2*, the 40 mol% A specimen gave a more complicated d.s.c. thermogram compared to those of the 50 and 60 mol% species, therefore we shall describe first the relatively simpler 50 mol% case. *Figure 4* shows the d.s.c. thermogram and the temperature dependence of the depolarizing transmittance of this compound. Two large endothermic peaks appear at ~177 and 200°C, with a small peak at ~226°C. The 177 and 226°C peaks were found to be related to the melting and isotropization transition processes of this compound, respectively. However, the peak at 200°C, which has a large enthalpy

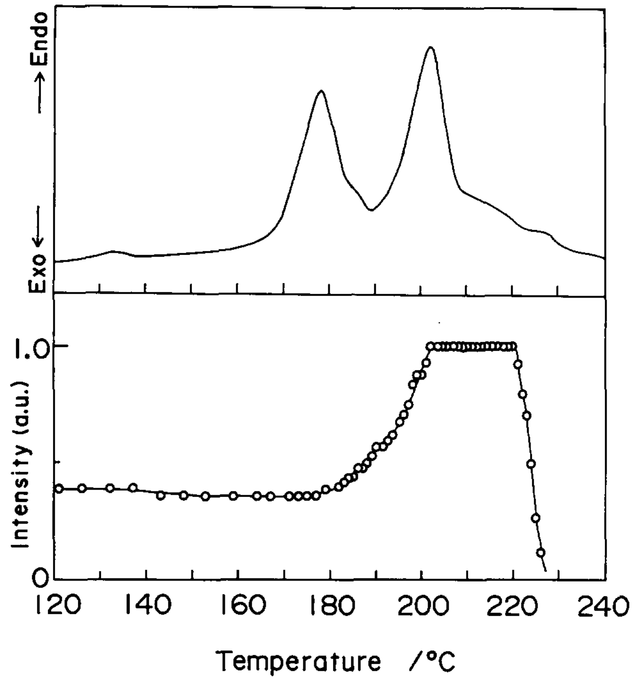

Figure 4 D.s.c. thermogram (top) and depolarizing transmittance curve (bottom) of the copolymer containing 50 mol% of component A

change, does not seem to originate from a transition occurring in the melting state, because such types of transition usually occur accompanied by very small changes in enthalpy. To identify this transition more clearly, we carried out further, careful optical microscopic observations. As seen in *Figure 5*, we found that the specimen is only partially melted and changes into the isotropic liquid below 200°C, and in this temperature region no meaningful change can be detected in the transmittance curve shown in *Figure 4*. With further increasing temperature, the other parts of the specimen start to melt to form the N phase, accompanied by a gradual increase in transmittance. After the latter melting at ~200°C the transmittance reaches a maximum and remains almost constant until the onset of the isotropization transition process of the N phase at ~220°C. In addition, X-ray diffraction measurements showed that in the solid state the diffraction pattern of this copolymer is essentially consistent with a superimposed pattern of the A and B homopolymers, as can be seen in *Figure 6*. Therefore, we presume that the A and B segments along the polymer backbones may separately form their own crystalline domains, which melt and then change directly into the isotropic liquid at ~177°C for the A component domains, but transform to the N phase at ~200°C for the B component species. This supposition is also supported by other d.s.c. and X-ray diffraction data: if the sample is heated to 186°C (at which temperature the first melting process is complete) and then subsequently cooled down to room temperature, the melted portions were never found to be recrystallized, and on reheating there could only be observed the second melting peak at ~200°C in the d.s.c. curve. Such a 'non-recrystallization' behaviour was very similar to that observed for the homopolymer A. Furthermore, this cooled sample gave only a diffraction pattern which was characteristic of the B component. In other words, miscibility between the two segments is not good enough to cause cocrystallization and co-liquid crystallization, regardless of their similar chemical structures. As in the case of the homopolymer A, the A component domains within the copolymers also exhibited no liquid crystallinity. To our knowledge, this seems to be the first case in which a microphase separation phenomenon has been observed in liquid crystalline copolyethers. Although the present copolymers were prepared by a random copolymerization process, the A and B components, however, seem not to be so random in segment length and distribution along the copolymer backbones, thus resulting in the occurrence of microphase separation for the different

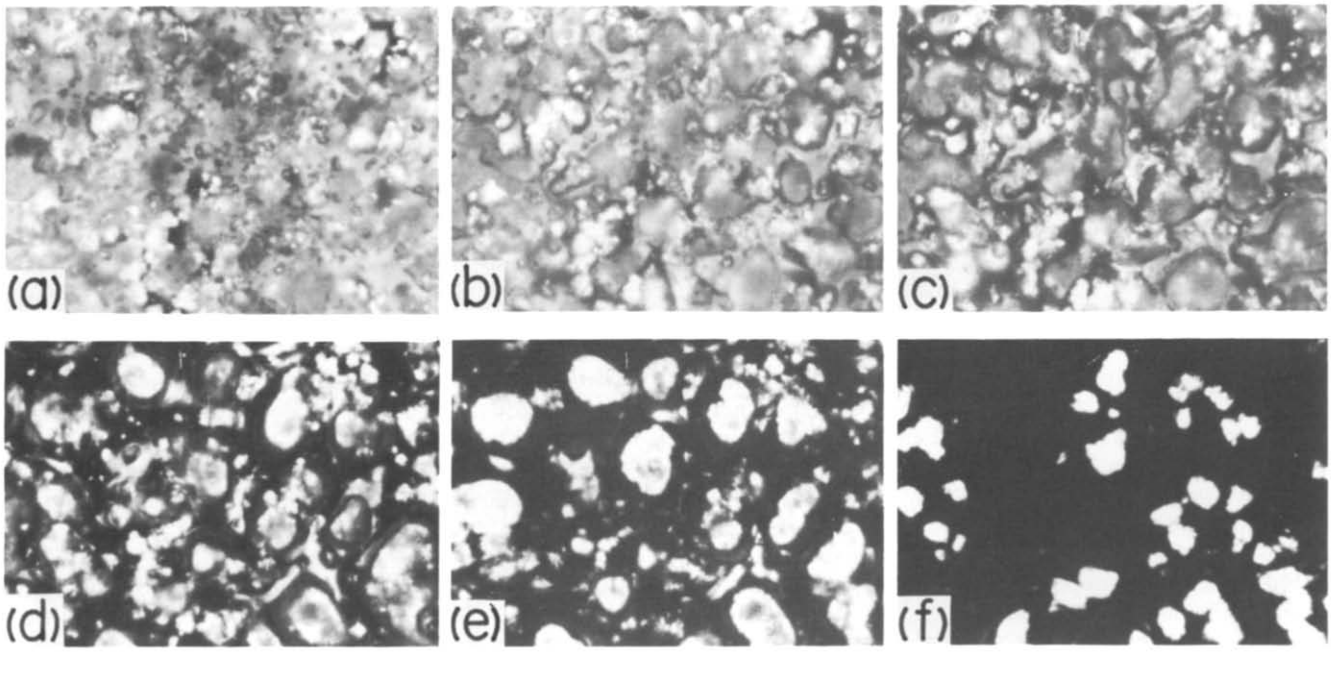

Figure 5 Optical micrographs of the copolymer containing 50 mol% of component A taken at different temperatures: (a) 174°C; (b) 187°C; (c) 192°C; (d) 200°C; (e) 206°C; (f) 220°C

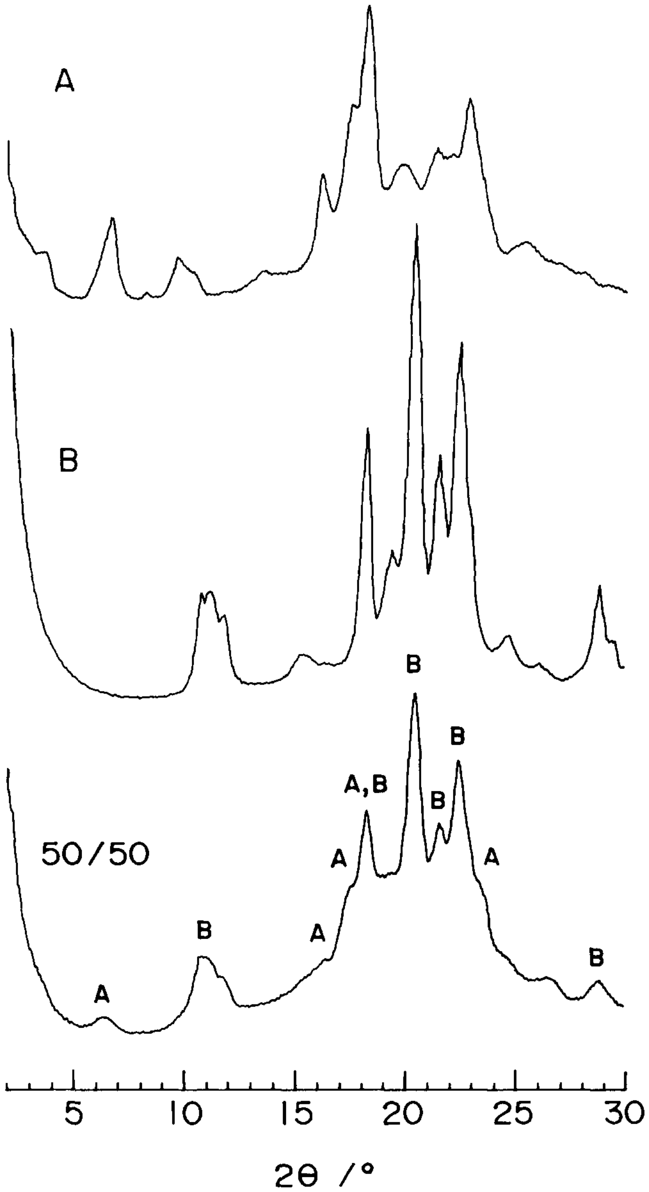

Figure 6 X-ray diffraction patterns of the A (top) and B (middle) homopolymers, and the copolymer containing 50 mol% of component A (bottom)

segments. This phenomenon is somewhat analogous to the case of the PET/PHBA copolymers, as described above. Furthermore, we found that the specimen containing 60 mol% of the A component may also exhibit phase transition and microphase separation behaviour, similar to that of the 50 mol% specimens.

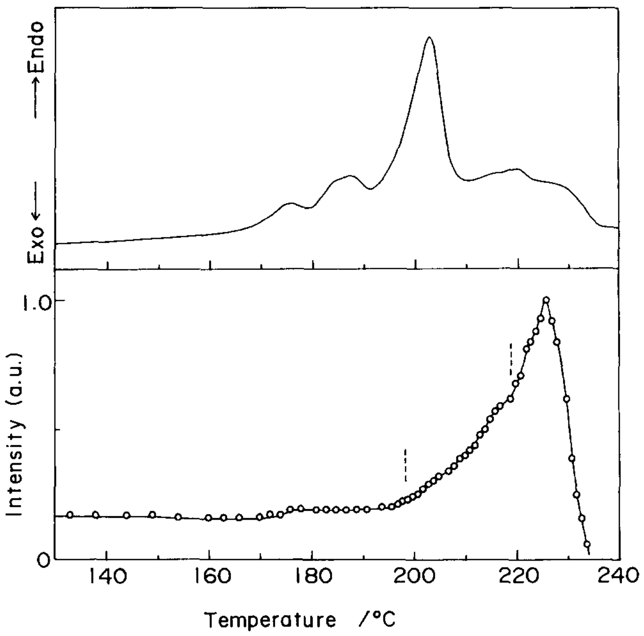

Figure 7 D.s.c. thermogram (top) and depolarizing transmittance curve (bottom) of the copolymer containing 40 mol% of component A

We shall next describe the phase transitions of the 40 mol% A component specimen which gave the more complicated d.s.c. thermogram. *Figure 7* shows its d.s.c. curve and the temperature dependence of its depolarizing transmittance. A total of five endothermic peaks can be observed, at ~175, 187, 203, 220 and 230°C. The transmittance starts to increase gradually and continuously at around the d.s.c. peak temperature of 203°C, while above 220°C it increases more rapidly and then reaches a maximum at ~225°C. We further made microscopic observations and found that melting of the sample and the transition process from its K to N phases are taking place over a broad temperature range of ~190–225°C. The 230°C peak corresponds well to the isotropization transition process of the sample. In order to clarify the structural changes that occur around each d.s.c. peak, we have further annealed the sample at different temperatures, because such treatment usually causes polymeric crystalline or semicrystalline domains to grow more completely and hence raise their melting temperatures[9,10]. *Figure 8* shows the d.s.c. thermograms recorded for samples annealed in this way. The original sample is represented by curve (a). After annealing the sample at a temperature corresponding to point A and

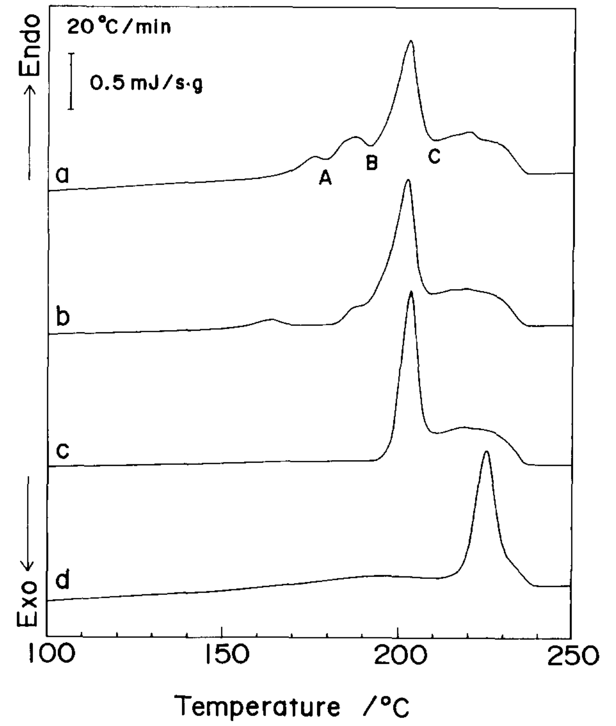

Figure 8 D.s.c. thermograms of the copolymer containing 40 mol% of component A, annealed under different conditions (see text for details of treatment)

then cooling down to room temperature, the subsequently rescanned d.s.c. curve (b) is produced. This annealed sample at first partially melts at around a d.s.c. peak of 165°C which is somewhat lower than that of the original sample (~175°C). We have also found in the case of homopolymer A that after cooling the original sample from its melting state the reheated sample will be melted at a temperature which is lower than its original one. This melting-point-lowering behaviour seems to be also applicable to the present copolymeric system. Therefore, we have supposed that the 175°C peak of the original sample in curve (a) is due to melting of the A component domains, which occurs at a value which is very close to the melting temperatures observed for the 50 and 60 mol% A copolymer samples, as well as the 100 mol% A homopolymer material. Except for the small peak at 165°C, the curve (b) is still similar in shape to curve (a), although some peaks have changed their heights slightly. Curve (c) was recorded for a sample which was annealed at a temperature corresponding to point B. In this curve, there appears no peak corresponding to the two occurring below the B point, while the peak at ~205°C is sharper and stronger in shape and appears at a slightly higher temperature, when compared with curves (a) and (b). This is perhaps due to more complete growth of the crystalline or semicrystalline domains during the annealing process. Within the temperature region above this largest peak, the curve shape is also very similar to that of both curves (b) and (a). With a further increase in the annealing temperature to that represented by point C, however, the d.s.c. curve was changed remarkably (shown in curve (d)). The peak at 203°C has largely shifted its position to 225°C, which is very close to the temperature at which the transmittance reached a maximum value (see *Figure 7*). Such a large shift in melting temperature was considered to originate from a more complete growth of crystalline domains after the sample was annealed in the mesomorphic state. As a result of these observations, we are inclined to believe that this new peak may be related to the actual melting process of the well crystallized and microseparated B component domains in this copolymer. In addition, the shoulder on the higher temperature side of this peak may be related to the isotropization transition process of this sample.

Specimens containing 80 and 100 mol% of component A

From microscopic observations, these two specimens were found to exhibit no liquid crystallinity in their melting states. This can be expected from the spatially non-linear geometry of the A monomer unit, as a result of the almost unchanged angle of the Ph–CH_2–Ph group. It was also found that these specimens may experience multiple melting processes on heating, as shown in their d.s.c curves (see *Figure 2*). Such phenomena may be related to a relatively wide distribution of molecular weights and are also probably due to different specific packing structures of the polymer chains existing in each specimen. The detailed structural changes will be further investigated and discussed in a future publication.

Phase diagram of the copolymers

From the above results, we have obtained the phase diagram for this series of copolyethers and this is shown in *Figure 9*. As shown by the broken line, the melting point of the crystal domains composed of A component segments, T_m(A), is changed very little with changes in the component content. For this curve, the T_m(A) values of the 80 and 100 mol% A specimens were plotted as the mean temperature between the two large melting peak temperatures on the low-temperature side of the d.s.c. curve (see *Figure 2*). The multiple melting phenomenon for the A component domains, however, could not be detected clearly in the d.s.c. curves of the 40–60 mol% A copolymers. This is probably due to somewhat of an overlap of the A melting peaks with those of the B component, or originates from a shortening of the A segment length in comparison to its homopolymer. On the other hand, as shown by the solid lines, the melting point, T_m(B), and the isotropization transition temperature, T_i(B), (which could not be detected clearly in the d.s.c. curves for the 20 and 60 mol% A specimens but was approximately evaluated from careful microscopic observations) of the B component domains is lowered significantly with decreasing B component content.

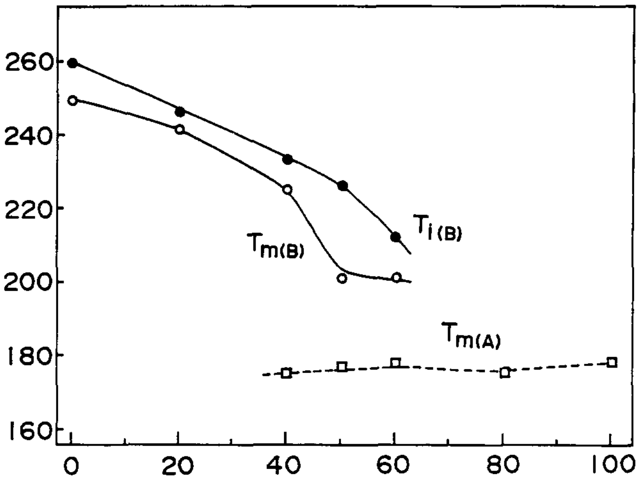

Figure 9 Phase diagram of the copolyether series

In this present copolymer system variations in the phase transition temperatures may be quite sensitive to changes in the molecular weights of each segment, or the segment length and its distribution along the copolymer backbones. From the results shown in *Figure 9*, it is supposed that most of the A segments may have relatively long lengths and the crystal domains aggregated by these segments may also be large, so T_m(A) is changed only slightly in comparison to that of the A homopolymer. In the 20 mol% A specimen the T_m(A) value could not be detected clearly, because the A component content is too low. On the other hand, the lengths of the B segments are rather short and decrease with increasing the A component, which results in a continuous drop in T_m(B). This means that the growth of the B unit sequence during the polycondensation reaction is easily interrupted by the A units, even when the content of A is as low as 20 mol%. The lowering in T_i(B) may also originate from a continuous shortening of the B segments, but one cannot exclude the possibility of interpenetration between the different segments in the melting state. At this time molecules are more fluid and the two different segments (with similar chemical structures) are possibly miscible to some extent with each other within the same mesophasic domain or isotropic region, thus leading to a lowering of T_i(B). However, the two factors affecting

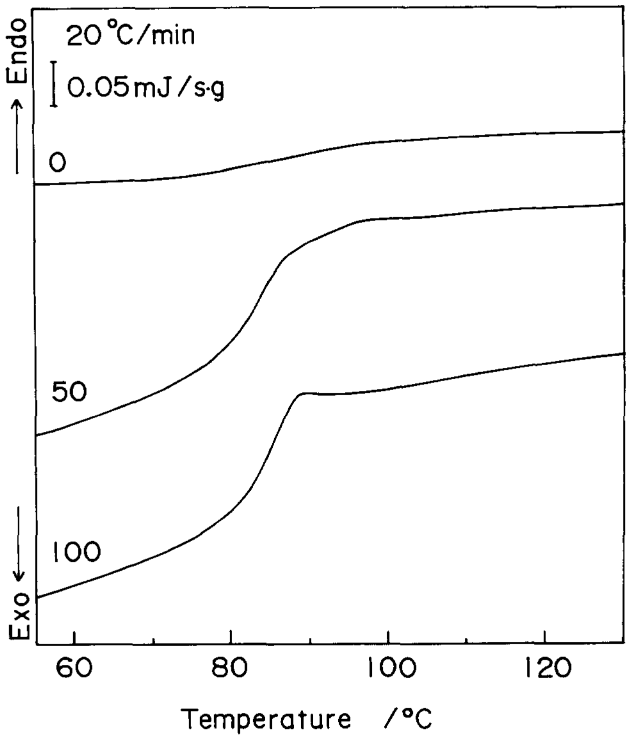

Figure 10 D.s.c. thermograms of samples of the A and B homopolymers and a 50 mol% A copolymer sample, which were subsequently reheated after cooling from their isotropic states

the transition temperatures were difficult to discriminate from each other in this work. In addition, as the two component segments are linked together along the polymer chains, the melting or isotropization transition of one of the component domains may also affect the thermal stabilities of the other domains. This effect can be largely regarded as a boundary interaction between the two domains, so it is not considered to be that significant.

We have discussed in detail the microphase separation behaviour for this copolymer system in its crystalline and liquid crystalline states. It is also very important to examine the miscibility between the A and B component segments in the amorphous phase below the glass transition temperature (T_g) and in the isotropic state above T_i. Unfortunately, this was not easy to carry out for the present system; for example, the T_g values of the A and B homopolymers are very close to each other (see *Figure 10*), due to their similar chemical structures and molecular fluidities. Only one T_g value was apparently observed for each copolymer, and this was also very close to those of the homopolymers. Therefore, it is necessary to further investigate the miscibility with other more powerful techniques in a future study.

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