

MORPHOLOGY OF BISPHENOL A POLYSULFONE-POLYOXYPROPYLENE SEGMENTED COPOLYMERS*

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ABSTRACT

Morphology of bisphenol A polysulfone-polyoxypropylene segmented copolymers was investigated by means of differential scanning calorimetry and transmission electron microscopy. The results show that the molecular weights of the hard and soft segments have a pronounced effect on the morphology of these segmented copolymers, which may change from three-phase to single-phase structure depending on the size and the relative size of the segments. Heat treatment will enhance the process of phase separation, increasing the domain size of the dispersed phase. Results obtained by study on the dynamic mechanical properties of these copolymers well support the existence of three-phase morphological structure.

It has been, recently, very active in the study of synthesis, morphology and properties of segmented copolymers, as these copolymers possess a variety of unique properties, and more over, they may be obtained simply by utilization of known monomers and proper copolymerization method. As already known, their properties are closely related to their morphological structure^[1-3].

This paper presents our study on the effect of the lengths of hard and soft segments on the morphology of bisphenol A polysulfone-polyoxypropylene segmented copolymers by means of differential scanning calorimetry (DSC) and transmission electron microscopy (TEM).

EXPERIMENTAL

The bisphenol A polysulfone-polyoxypropylene segmented copolymers with different molecular weights (*MW*) of hard and /or soft segments (BPS-I-N, M, where N representing the *MW* of polysulfone, M that of polyoxypropylene) were synthesized in this laboratory with 4,4'-diphenylmethane diisocyanate (MDI) as bridges between the hard and soft segments. The method of synthesis and the characterization of the copolymers were reported in a previous paper^[4].

The calorimeter used was Perkin-Elmer DSC-2C, temperature range 120—523K, heating rate 20K/min, and sample weight was about 15 mg.

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The electron microscope used was Hitachi H-500, accelerated voltage 100 kv. Thin film specimens were prepared by solution casting with tetrahydrofuran (THF) as solvent and 0.5% concentration.

RESULTS AND DISCUSSION

Owing to its high sensitivity and relatively simple operation, DSC has already been widely used in studying the thermal properties of segmented copolymers, especially the various transitions, in order to study their multiphase morphological structure, compatibility and phase separation of the hard and soft segments.

As the temperature range covering the transitions of these copolymers is rather wide, and for convenience, the DSC runs were carried out separately with two, lower and higher, temperature ranges. Figure 1 shows the DSC thermograms thus obtained, where A and B are the

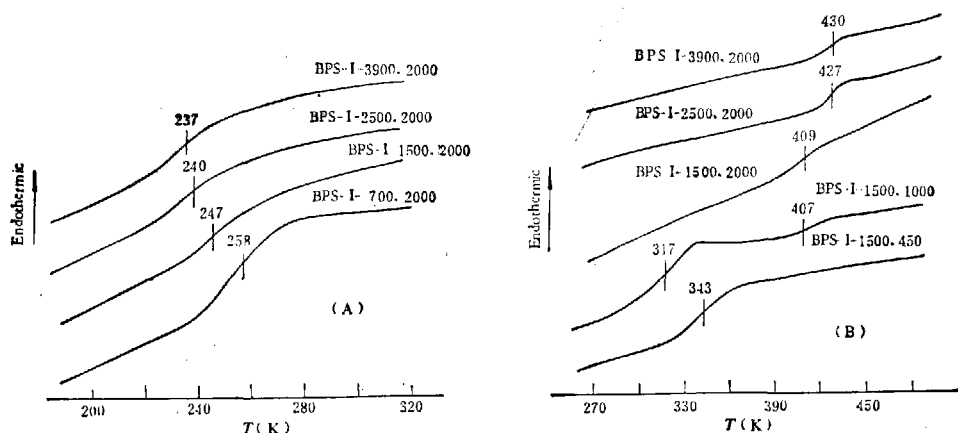


Fig. 1 The DSC thermograms of samples of BPS-I series
(A) lower temperature range; (B) higher temperature range.

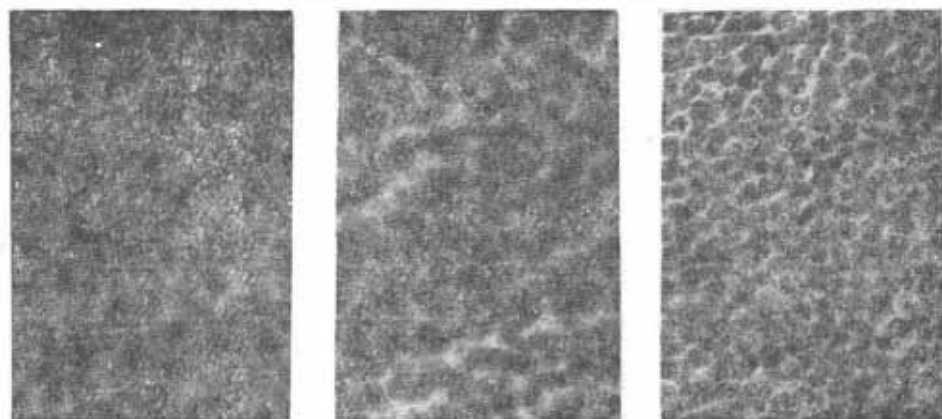
lower and higher temperature ranges respectively. From these curves it may be seen that with the exception of samples BPS-I-700,2000 and BPS-I-1500,450, the rest four samples all had two transitions, one in the lower temperature range, the other in the higher temperature range. According to our DSC study on the corresponding oligomers^[5], the lower transitions may be assigned to the glass transition (T_g) of the soft segments, polyoxypropylene (POP), while the higher one is the T_g of the hard segments, bisphenol A polysulfone (BPS). This indicates that these four samples all had two-phase structure. For BPS-I-700,2000, there only exists one transition on the lower temperature range DSC curve, which should be the T_g of POP. It is considered that the absence of BPS's T_g is due to that its MW was too small to aggregate, hence not possible to form big enough domains but dispersing as segments or micro-aggregates in the soft segment phase, thus resulting in "apparent compatibility" with the soft segments. This was further proved by the fact that two-phase structure did not show up under TEM observation. On the other hand BPS-I-1500,450 had only one higher temperature transition,

343K, as its soft segments were not able to form domains due to the same reason. Again, no two-phase structure was observed under TEM.

It is noticed that, in Figure 1A, the T_g 's of the soft segments of all the samples are higher than that of their oligomers, which is 206 K^[5], and the differences are quite big, being as much as 30—50K. It is believed that this pronounced shifting of T_g to higher temperature is due to the strong action given by the hard segments through covalent bonding in addition to normal interaction between the hard and soft segments. Another phenomenon noticed is that when the MW of the soft segments was fixed at 2000, the T_g of the soft segments decreased with the increase in the MW of the hard segments from 700 to 3900. This might be resulted from that the compatibility of the two different segments decreased with the increase in hard segment's MW , which made more and more hard segments aggregate to form domains and then the soft segment phase contained less and less hard segments, thus decreasing the interaction between the hard and soft segments in the soft segment phase and hence decreasing the elevation of its T_g and making it nearer and nearer to the T_g of its oligomer.

It should be pointed out that the curves in Figure 1B show that the hard segment T_g 's are close to or even higher than the corresponding oligomer's T_g . The foregoing explanation seems not applicable to this phenomenon. However, by further analysis of the samples, it is easy to tell the cause. As mentioned, in this BPS-I series, MDI was used as the bridges between the hard and soft segments. The molecular structure of MDI is similar to that of the hard segments; at the same time MDI and the hard segments were joined together through PU segment. This not only gave rise to the possibility of hydrogen bonding formation between the segments, but also to the effect of increasing the length of the hard segments. A calculation of the T_g of the hard segment with MDI as a part of its chain according to the empirical equation for hard segment ($T_g = 462 - 8.07 \times 10^4/M$)^[5] would give higher T_g 's than those obtained for hard segments in the copolymers.

However, when the MW of the hard segments was fixed at 1500, with the decreasing of the MW of the soft segments from 2000 to 450, the copolymer showed two T_g 's first and then one



(A) BPS-I-1500,2000 (B) BPS-I-2500,2000 (C) BPS-I-3900,2000
Fig. 2 TEM micrographs of samples of BPS-I series (48 hrs. at 80°C, under vacuum)
Magnification: 8000×2.

T_g at 450; and the temperature range of the soft segment T_g shifting was rather wide, from 247 to 317 K. Comparing these two cases, it seems that it is easier to change the degree of phase separation by changing the MW of the soft segment.

In Figure 2 are TEM bright field micrographs of three of the BPS-I series samples, which were heat-treated at 80°C under vacuum for 48 hrs. All these micrographs show two-phase morphological structure. However, with careful examination, the existence of three different kinds of domains, black, grey and bright, may be seen. For these samples, the hard segments were composed of benzene ring with π -electron and sulfur of high atomic order, while the soft segments were composed of carbon, hydrogen and oxygen. So the electron density of the hard segments is much higher than that of the soft segments, making the hard segment's power of scattering incident electrons stronger. Therefore, the black domains should represent the hard segment, BPS, phase, the bright domains the soft segment, POP, phase. However, in the case of segmented copolymers, it is reasonable to consider that, due to molecular structure, pure phase could hardly exist. Therefore, in this case, the black domains are not composed of only hard segments, but mixed with very small amount of soft segments, i.e., hard segment, BPS, rich phase. For the same reason, the bright domains represent the soft segment, POP, rich phase, while the grey domains should be a mixed phase with BPS and POP near to each other in composition. It may be seen from the micrographs that when the MW of the soft segments was fixed, the two-phase structure and the phase boundary got more and more distinct with the increase in the MW of the hard segments, while the mixed phase gradually diminished, showing that the compatibility and phase separation between the soft and hard segments decreased and enhanced respectively as the MW of the hard segments increased. These results are in good agreement with that of DSC. However, the dispersed microdomain size of the hard segments did not change much with the change of its MW , being within the range of 800–1200 Å. The reason for this fact might be that, as mentioned above, the hard segment domains were not pure but with soft segments as occlusions, which was clearly seen under TEM of high magnification, as shown in Figure 3. This, we consider, is the characteristic of the morphological structure of segmented copolymers.

Figures 4 and 2C are TEM micrographs of the same sample with same EM and optical magnifications, but different in heat treatments, one 48 hrs at room temperature (Fig. 4), the other



Fig. 3 TEM micrograph of BPS-I-3900,2000
Magnification: 40000 $\times$ 2.

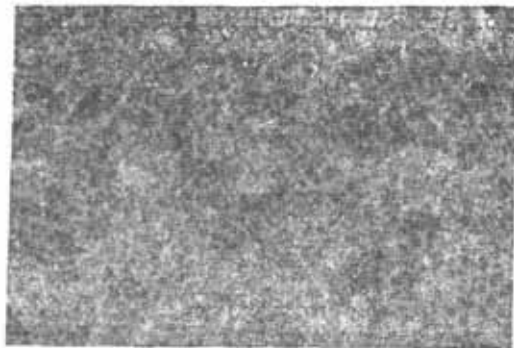


Fig. 4 TEM micrograph of BPS-I-3900,2000 (after 48 hrs. aging at room temperature)
Magnification: 8000×2

48 hrs at 80°C under vacuum (Fig. 2C). It is evident that the hard segment microdomains after 48 hrs heat treatment at 80°C (Fig. 2C) are much larger than those with no heat treatment (Fig. 4), which suggests that proper heat treatment will enhance phase separation, therefore changing the morphology of the sample.

Two-phase structure was not observed for the rest three samples. The possible reason for single-phase structure and the existence of only one T_g for samples BPS-I-700,2000 and BPS-I-1500,450 was discussed in the foregoing sections. But for sample BPS-I-1500,1000, there existed two T_g 's on its DSC curve, which, we think, might be due to the low MW 's of the hard and soft segments and their small difference. These might result in the formation of two mixed phases, with one or the other segment as major component, but very small difference in composition. Under such conditions, the contrast between these two phases may be too small to be observed under TEM.

Furthermore, the results of our TBA study of these samples well support the three-phase morphological structure existing in some of them as obtained by DSC and TEM study. The dynamical mechanical property vs. temperature curve of BPS-I-3900,2000 is taken as an

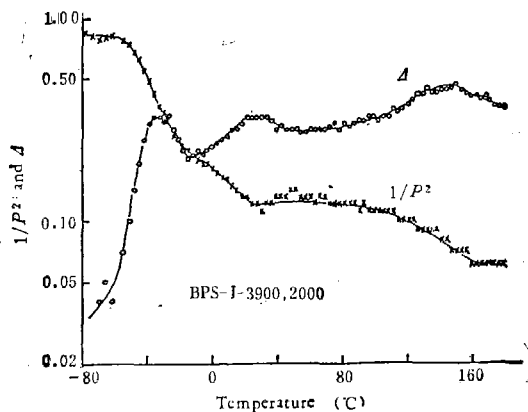


Fig. 5 Plot of $1/P^2$ and Δ vs. temperature
BPS-I-3900,2000

example shown in Figure 5. It is very clear that three loss peaks appeared on the log decrement curve at -40 , 20 and 150°C corresponding to the T_g 's of POP rich, POP and BPS mixed, and BPS rich phases respectively. A study on the dynamic mechanical properties of these segmented copolymers will be reported in another paper.

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