# Microphase Separation in Solutions of Crystallizable Segmented Polyurethane

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SUMMARY: At present time the level of microphase separation together with polymer nture is considered to be a main factor in determining the physico-mechanical properties of polyurethane materials. The researches show that realization of a certain polymer structure and properties of polymer are defined by microstructure of polyurethane chain.
The purpose of this work was to study physico-chemical regularities between nucleation and growth of microphase aggregations in crystallizable segmented polyurethane compstions as a function of the phase state of the system during transferring from comon solvent to a selective solvent. Besides we investigated the architecture of macromolecules, associates and phase particles of segmented polyurethane (SPU) formed in different regions of the phase diagram.

## Experimental

The basic difficulties arising at research of SPU are connected to incompleteness of a phase separation in these systems. It is this feature of the structural-morphological behavior of SPU that is believed to account for a dependence of their properties on the thermal prehistory and the processing conditions.

Our investigation was performed on the samples of SPU with a molecular weights of $2x10^{-4}$ (sample PU) synthesized from a polyester poly(ethylenebuteneadipate), diphenylmethane diisocyanate, and 1,4-butanediol as a chain extender. The molecular weights of both soft (flexible) and hard segments in PU were about 2000. Dimehtylformamide (DMF) was used as a common solvent for both polyurethane blocks, and ethylacetate (EA) served as a selective solvent for the flexible block and a precipitant for the hard block.

The main objective in determination of the level of macro and microphase changes in ternary systems was in selecting methods allowing to distinguish the changes occurring at different levels of molecular structure, both in the polymer block and in solution. Mainly microphase changes were studied by means of rheological methods [1,2]. Specific interactions of solvents with blocks on mcro and macro levels of phase separation were investigated with the help of DSC [3] and trasmision electronic microscopy (EM-301 Philips). Amorphous separation in the systems PU-DMF-EA was studied by turbidimetric titration, turbidity spectrum

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measurements, and PU film swelling in EA-DMF mixtures of various compositions. The equilibrium of crystalline phases in the same systems was studied by determining the appearance of spherulites in the course of solvent evaporation in a NU-2E polarization microscope equipped with a special cell.

## Results and Discussion

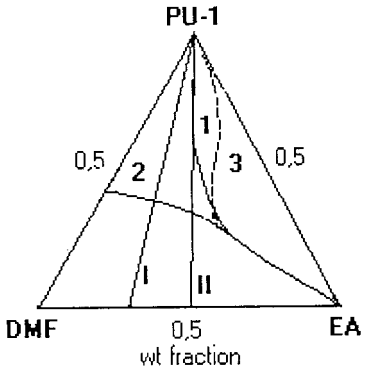


Figure 1. Phase diagrams of the PU-DMF-EA system: (1) binodal; (2) liquidus; (3) spinodal; (I) area of molecular conformational reorganization of the macromolecules and (II) area of intramolecular conformational reorganization of the macromolecules.

Fig. 1 shows the phase diagram of the system PU-DMF-EA [1,2]. One can see that the diagram shows a combination of two types of phase equilibria, namely, amor phous separation and crystal equilibrium. From the point of macroscopic view, the phase diagram has rather a simple form: the binodal is smooth curve convex in the direction of the composition axis of the binary system PU-DMF, while the zone of amorphous separation occupy rather large area on the diagrams. The area of PU solution is intersected by the liquidus curve which is convex in the direction of the PU-EA axis; this curve separates the true solution area from the area where two crystalline forms of PU coexist.

What transformations does a macromolecular coil undergo in dependence on the phase state of the composition? In order to answer on this question, let us have a look on phase diagram in detail and, first of all, on the amorphous phase separation.

In the area of dilute solutions, the binodal and spinodal curves practically coincide, so phase separation in PU-DMF-EA systems with an increase of EA content goes through spinodal separation mechanism. Hence changes in the size of macromolecule coil in dilute PU solutions can be known from intramolecular transformations caused by solvent content. The changes in the coil size of a PU molecule were estimated using capillary viscometry [2]. The results of the studies are presented in Fig. 2. It is evident that the PU macromolecules have the largest coil size in DMF and the smallest coil size in the mixed solvent. Ethyl acetate is selective solvent for the flexible block and a precipitant for the hard block [4]. Compression

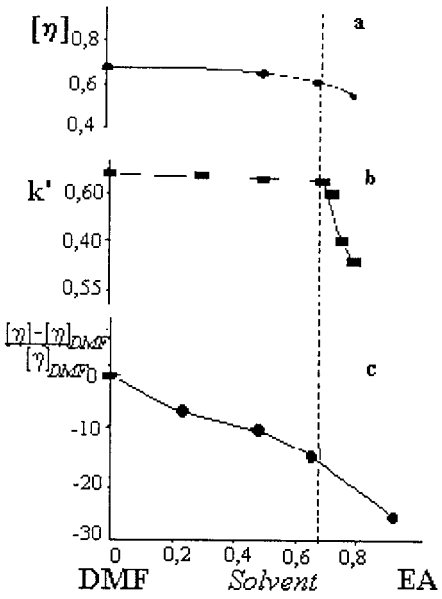


Figure 2. The plots of (a) intrinsic viscosity [h], (c) relative volume of the macromolecular coil of PU; (b) viscometric Huggins constant k' of PU solutions versus the solvent composition.

of macromolecule coil at an in-appreciable modification of Huggins constant with increase in the EA content happens from diminution of volume occupied by hard segment. We calculated the number of blocks required for the formation of associates inside a macromolecule. One can see in the Fig. 2 that the transition of PU-DMF-EA compositions into a two-phase system is observed at EA content close to 30 % in the mixed solvent and at macromolecule compression by 12%. This corresponds to the formation of associates consisting of 3-4 hard blocks on average, with critical volume about 2600-3470 Å$^3$, inside the macromolecule coil. Further deformation of molecular coil is possible only if associates of hard blocks are formed at an intermolecular level.

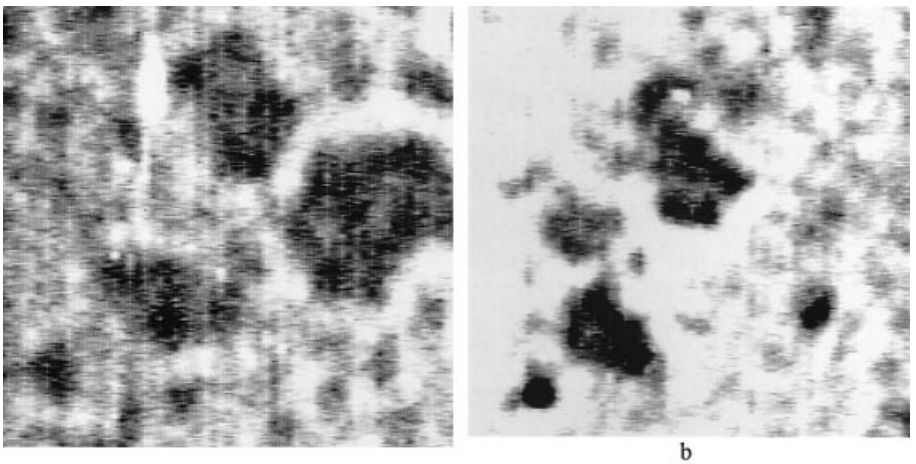


Figure 3. Micrographs of mono-, di-, tri-, tetra- and hexameric particles of PU macromolecules formed from 0.03% solutions in DMF (a) and DMF: EA = 1:0.5 (b) on a graphite support. Magnification x 440,000.

Electron micrographs were made for separate macromolecules and their associates obtained from 0.03% PU solutions [4]. The results of these observations are presented in Fig. 3-5. The micro-graphs were processed by means of Image Expert graphics software which provided additional control of the quality of photographic images, scaling, evaluation of optical density changes over the object cross-section (Fig. 3,4) and 3-D imaging of the object (Fig. 5). By observing the photographic plates, we located fragments whose sizes corresponded to macromolecules, associates, and phase particles, and analyzed these fragments.

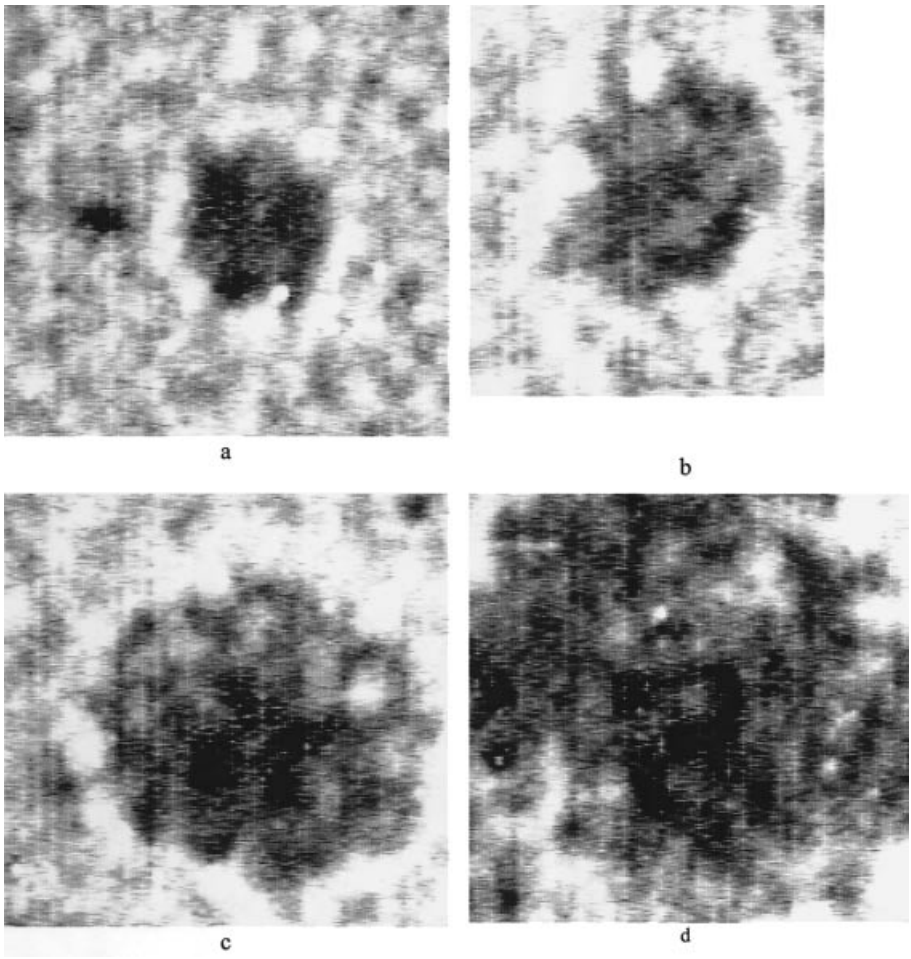


Figure 4. Micrographs of SPU particles formed from solutions in DMF on graphite support; the particle sizes correspond to associates (a-c) and phase particles (d) of macromolecules. The plane plotting. Magnification x 440,000.

Fig. 3 gives a good illustration of the compression of molecular coils and associates of PU molecules as the solvent composition is changed from DMF (a) to DMF:EA = 1:0.5 (b). The dense molecular coils in the DMF:EA = 1:0.5 mixture form the more compact and dark structures on the support; the surface area of these structures is approximately surface area of these structures is approximately 35% smaller than that of the corresponding structures formed from DMF. It should also be noted that the simplest associates consisting of two, three, four or at most six molecules do not display the significant structural changes caused by segregation of the PU chain hard blocks that we observed by capillary viscometry; however, the abrupt optical density changes across the particle diameters indicate that there are some changes comparable to experimental errors.

As the particles grow, the observed effect of segregation of the PU chain hard blocks increases (Fig. 4, 5). We estimated the optical density of particle images over the cross-sections passing through their diameters and recorded significant density fluctuations. These fluctuations probably result from changes in the macromolecule block microstructure.

As the particle size increases, the optical density fluctuations become more pronounced, and certain structural regularities can be noted (Fig. 4,5). Taking the rheological results into consideration, one can say that in small PU particles whose sizes correspond to those of associates, the hard blocks play the role of organizing elements (Fig. 4a-c, 5a-c) by displacing the flexible blocks and thus favoring their organization. The mosaic structure of the particles is likely to originate from the alternation of associated hard and flexible block regions. The architecture of these particles is determined by the diameter and thickness of the particle owing to the flexibility of the macromolecular chain, which imposes restrictions on the spatial arrangement of the segregated regions. As the size of the segregated regions in the blocks increases, the particle architecture changes.

Probably, a criterion of transformation of an associate to a phase particle includes the formation of lamellar fragments (Fig. 4d, 5d) observed as stretched and narrow structures with sharp contrast changes. The existence of crystal ordering in the particles is supported by the electron diffraction on these particles. Unfortunately, the low melting point of the flexible block (28-31°C) results in the fast melting of the crystals [3]. For this reason, we were unable to detect the diffraction on the photographic plate. Rheological studies of average concentrated compositions have shown [1,2] that in this concentration, movement of the figurative point over the phase diagram from DMF to EA correspond to abrupt changes in the supermolecular structure of the compositions. A calculation of activation energy of viscous flow has shown that the strength of interstructural bonds is minimal if the EA content in the mixed solvent is up to 30 % [2].

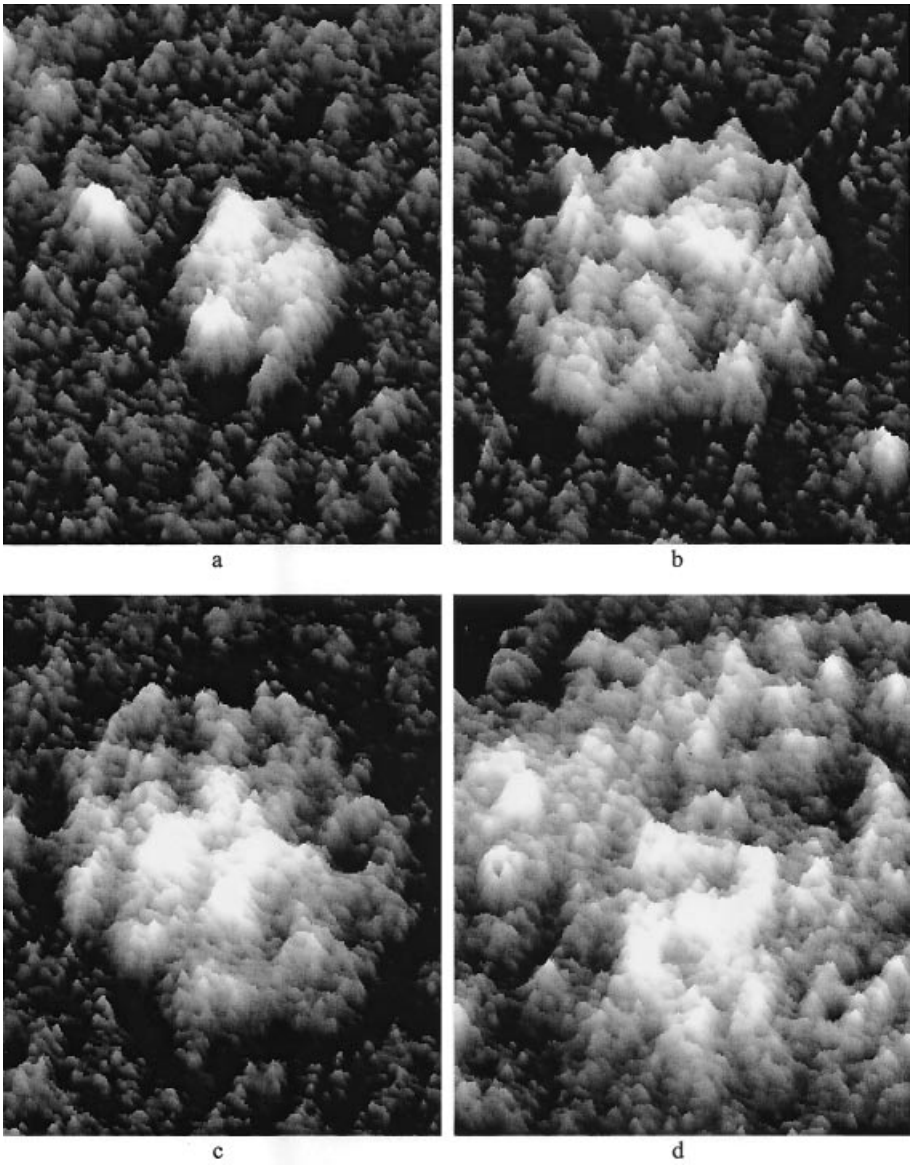


Figure 5. Micrographs of SPU particles formed from solutions in DMF on graphite support; the particle sizes correspond to associates (a-c) and phase particles (d) of macromolecules. The volumetric plotting. Magnification x 440,000.

Let us compare these results with the data obtained for dilute solutions. A decrease in interaction energy between the macromolecule coils in concentrated solutions at 30% EA in

the mixed solvent in dilute solutions corresponds to the maximal deformation of the macromolecule coil because of internal configuration capabilities.

Let us consider the crystal equilibrium. The crystal structure was studied during the formation of materials from dilute solutions, i.e. in the absence of interaction between the macromolecules, and in concentrated solutions, i.e. with contact between the macromolecules. Investigations have shown that the spherulite size decreases slightly with increase in the EA content; for example, it is 0,4μ in DMF and 0,2μ in a DMF:EA (2:1) mixture in the PU films which was obtained in the absence of interaction between the macromolecules.

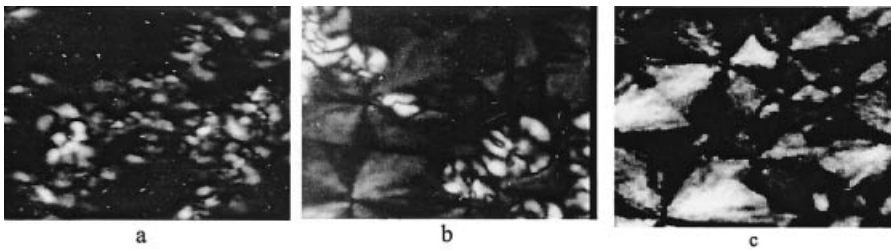


Figure 6. Micrographs of PU-1 spherulites obtained from solutions with various contents of the solvent (%): 20(a); 15(b); 4(b); (c) <1%. Magnification ×600.

Fig. 6 shows the composition structure during film formation. It is evident that structure formation occurs in two stages. Small liquid crystal spherulites with an average radius about 3 μ and a low melting point are formed in the first stage. They are easily deformed at ambient temperature, going into the tension zone. While the solvent is being removed, the liquid crystal aggregations are gradually recrystallized into spherulites with higher melting point and greater radius (up to 50 μ) [3]. Apparently, at the first stage the spherulites are organized as ordered hard segments of the polyurethane chain with a matrix of solvent molecules and flexible blocks. A study [2,3] of crystallization showed that the introduction of EA into the solvent composition displaces the beginning of the first stage towards lower polymer concentration. As the system approaches the binodal curve, the time lag between the first and second crystallization stages decreases [4].

Fig. 7 shows the structure of the films obtained from concentrated solutions of different composition. In a good solvent (DMF), spherulites are formed from distinct crystallites oriented along the spherulites based on stretched lamellas. It is interesting that the most perfect crystals (when the lamellas thickness is minimal) are from the compositions containing about 30% EA [3].

The study [3] of films with differential scanning calorimetry showed that changes in the glass transition temperature of the flexible block pass through an extremum. The maximum decrease in the glass transition temperature is observed for films formed from the solvent containing 30% EA. These films are also characterized by increased total melting enthalpy and crystal packing density of the flexible and hard blocks [3].

Thus, the results of studies of the crystal and amorphous phase separation are in agreement with each other. Also they suggest that similarity of the supermolecular structural elements formed in dilute solutions and in the polymeric block after removal of the solvent is preserved, both in the amorphous and in crystal areas. The next Fig. 8 shows a model for the nucleation and growth of microphase aggregations on changing the solvent composition. All of the previous models [5-7] for the structure of segmented PU's implied that microphase aggregations were formed only at the intermolecular contact level.

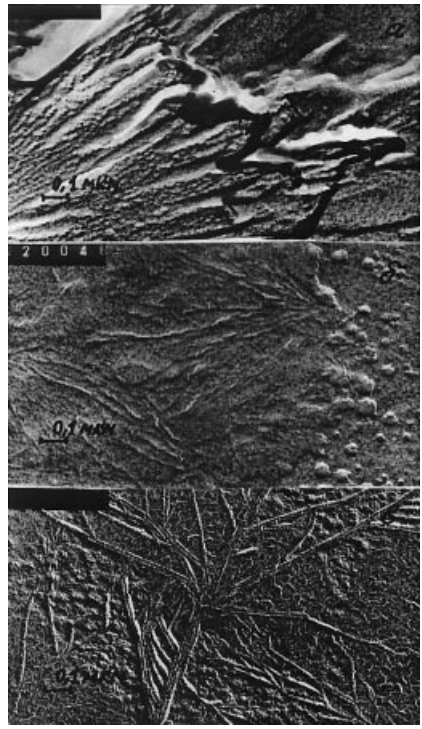

Figure 7. The structure of PU-1 samples obtained from 15% solutions in DMF (a), a DMF-EA mixture 0,33:0,67 (b) and 0,25:0,75 (c), w/w. Magnification ×59000.

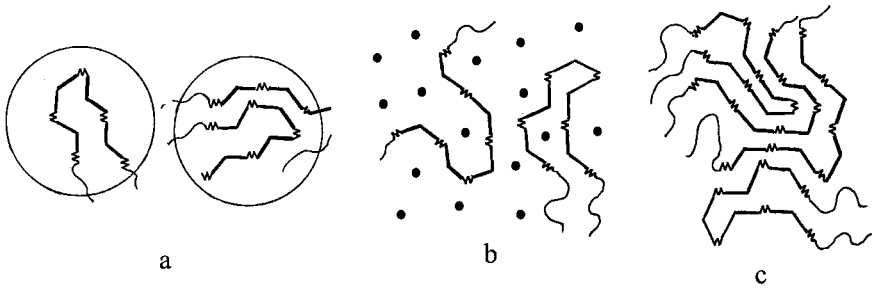


Figure 8. Model for the nucleation and growth of microphase aggregations: (a) microphase aggregations are nucleated at a level of separate macromolecules; (b) microphase aggregations are nucleated in solutions at the intermolecular contact; (c) microphase aggregations at the polymer.

~ – hard block; ~ – flexible block, • – molecules of the solvent

Thus, our studies show that microphase aggregations have been already nucleated in dilute solutions at a level of separate macromolecules. The suggested by us concept allows to distinguish areas with different mechanisms of microphase formation in the phase diagrams (Fig. 1). In the area limited by the axis PU-DMF and the straight line 1, we observe a continuous increase in the deformation of the polyurethane macromolecular coils because of the intramolecular conformational reorganization of the macromolecules. The crystal structure of the films formed in this composition range is characterized by continuous decrease in the thickness of the crystal lamellas. In the area limited by straight lines 1 and 2, additional deformation of the macromolecular coils occurs because of their association on the hard blocks. This results in a modification of the morphology of crystal aggregations - besides spherulites formed by extended lamellas, there appear separate crystallites, and the lamella thickness starts to grow slightly. In the area between the straight line 2 and the PU-EA axis, film formation occurs through the stage of amorphous phase separation. The crystal structure of films changes: separate crystallites are mainly formed.

Thus, the suggested model of the nucleation and growth of microphase aggregations in crystallizable PU's explains the structure changes and opens up new prospects for controlling the size of microphase aggregations.

References

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