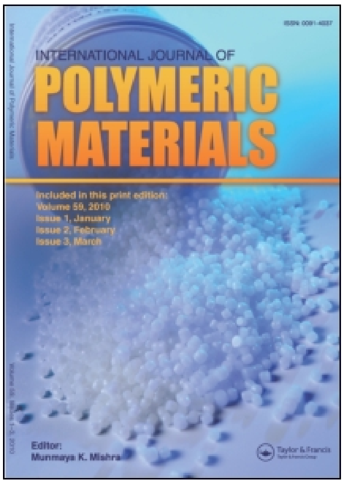

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

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Yuri S. Lipatov[a]
[a] Institute of Macromolecular Chemistry, Ukrainian Academy of Sciences, Kiev, USSR

To cite this Article Lipatov, Yuri S.(1992) 'What Are Blends and Alloys of Linear Polymers?', International Journal of Polymeric Materials, 17: 1, 91 — 92
To link to this Article: DOI: 10.1080/00914039208041102
URL: http://dx.doi.org/10.1080/00914039208041102

Intern. J. Polymeric Mater., 1992, Vol. 17, pp. 91–92
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What Are Blends and Alloys of Linear Polymers?

YURI S. LIPATOV

Institute of Macromolecular Chemistry, Ukrainian Academy of Sciences, 253160 Kiev, USSR

(Received August 29, 1991)

KEY WORDS Blends, alloys, phase diagrams, thermodynamics, polymers.

The expression "polymer blends and alloys" is widely used at present. However, until now there is no precise wording to describe what kind of binary or multicomponent mixtures should be referred to as "polymer alloy" and what kind of "polymer blend." Even in the recently published superb and fundamental book by Utracki,[1] only qualitative descriptions are given. Our aim is to propose definitions of the concepts "polymer alloy" and "polymer blend" based on thermodynamic considerations, taking as a basis the analysis of phase diagrams of binary mixtures.

It is known that the most common and convenient method of mixing two polymers is by melt blending, which is typical for metallic alloys. Alloys are macroscopically uniform substances obtained by fusing two or more metals, non-metals and organic compounds. In general, alloys are not obtainable by simple mechanical mixing of the components. By fusing, the components may form mixtures of various phases. The phase state of alloys in equilibrium may be determined from phase diagrams.[2] It is known also that for linear polymers the phase diagrams are of two types, with upper and lower critical solution temperatures (UCST and LCST). These are schematically described in Figure 1. Taking the phase diagrams as a basis, we propose the following definitions:

1) Alloys of linear polymers are binary or multicomponent systems that when mixed in the molten state are situated in the region of the phase diagram corresponding to mutual miscibility of the components and to the formation of one-phase solution. This means that the system is thermodynamically stable (at equilibrium) in the molten state. By cooling the melt a structure develops which depends on the thermodynamic state at a given temperature. If by cooling, a system with UCST enters the region at unstable states in the phase diagram (thermodynamic incompatibility arises), then the structure is a two-phase one and is determined by the conditions of phase separation. This structure will depend on the degree of phase separation and on the mechanism (nucleation or spinodal decomposition) of the separation process. The ratio and composition of the two phases, too, will be determined by the kinetics and mechanisms of phase separation. For binary systems with UCST the mixing should be conducted above the spinodal and for systems with LCST below the spinodal, i.e., in the region of one-phase solution. For systems

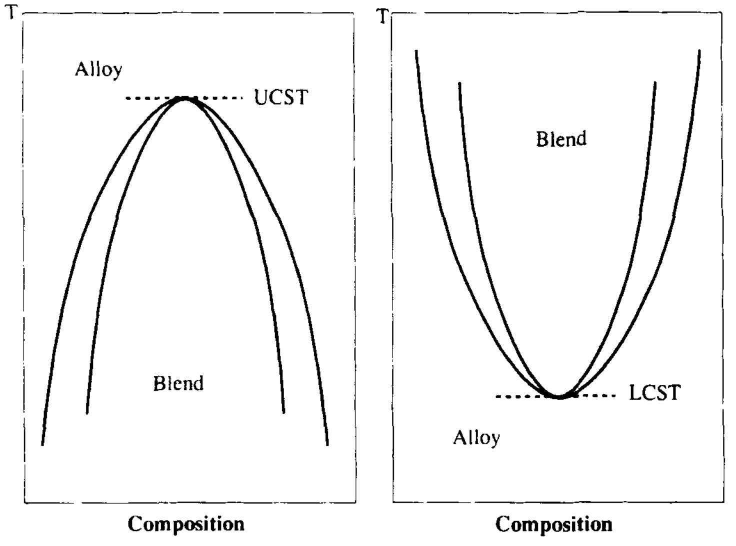

FIGURE 1 Phase diagrams of two-component systems as function of temperature. Left panel: system with UCST. Right panel: system with LCST. Interior curves: spinodal. Exterior curves: binodal.

with LCST, the one phase structure is preserved by cooling: a compatible system is maintained.

2) Blends of linear polymers are such binary systems which by mixing in the molten state are not miscible and do not form one-phase systems (they are thermodynamically incompatible). The components forming a blend may also have UCST and LCST. For systems with UCST, the formation of a blend proceeds at temperatures below the binodal and for systems with LCST above the binodal. The transition from two-phase to one-phase state for systems with LCST is practically impossible by lowering the temperature because of the high viscosity of the melt and the slowness of the mutual dissolution process. Thus, the structures of blends are determined by the degree of dispersion of one or both components achieved during mixing in the melt. This state is frozen by cooling the melt.

In such a way, depending on the temperature range of mixing relative to the position of the binodal and spinodal, the same polymer pair may form both alloys and blends. The realization of both possibilities depends on the relationship between the temperature of phase separation for a given composition of a mixture and the glass transition temperatures or melting points of both components.

As the formation of blends or alloys by fusing the components (mixing in the molten state) is always followed by temperature reduction, the definition given above allow to distinguish between the structural features of polymer alloys and blends. The analysis made above allows the conclusion to be drawn that two-phase or multi-phase blends are typical of systems with UCST, whereas one-phase alloys for systems with LCST.

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2. Physical Encyclopedic Dictionary; Soviet Encyclopaedia, Moscow, 1984.